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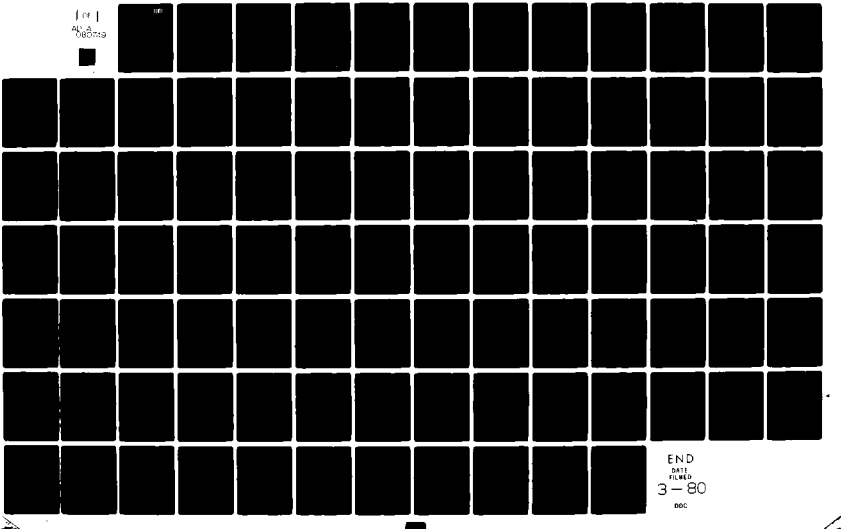

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Final Report for period 1 June 1978 — 30 June 1979

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This report describes the preparation of (a) diamantane, (b) exo-tetrahydrotricyclopentadiene, (c) the hydrogenated product of isomerized endo, endo-di(norbornadiene), and (d) some precursors of polyalkyldiamantanes.

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SUMMARY

This report describes the preparation of: (a) diamantane, (b) exo-tetrahydrotri(cyclopentadiene), (c) the hydrogenated product of isomerized endo, endo-di(norbornadiene) and (d) some precursors of polyalkyldiamantanes -- all excellent candidates for high energy hydrocarbon fuel formulations.

(a) Diamantane was prepared in a two-step process involving the hydrogenolysis of Binor-S using a 5% rhodium catalyst at 260°C and 429 psig to yield 96% tetrahydro Binor-S. This intermediate was isomerized with aluminum chloride at 65°C to yield 75% "raw" diamantane which may be recrystallized from toluene to obtain a 99% pure product.

(b) Trimers of cyclopentadiene were synthesized by heating endo-cyclopentadiene dimer at 170°-200°C and autogenous pressures for 7-10 hours. Vacuum distilling the resultant product isolated trimers boiling 115°C-132°C at 0.4 mm Hg which were 37% of the oligomeric mixture. These olefins were saturate using 60% nickel on Kieselguhr at 147°C and 197 psig hydrogen to yield endo-tetrahydrotri(cyclopentadiene)s. The latter, with 9% aluminum chloride in conjunction with hydrogen chloride, was isomerized at 0°-20°C to obtain an 81% yield of "raw" exo-tetrahydrotri(cyclopentadiene)s. This was purified by distilling the fraction boiling at 81°-108°C and 0.04-0.09 mm Hg pressure.

(c) Isomerization of the endo, endo dimer of norbornadiene with 10 weight percent acid-washed alumina at 170°-190°C yielded olefins which may be fully saturated using 10% nickel on Kieselguhr at 113°C and 100 psig hydrogen. This product is a mixture of hexacyclic isomers having a melting point approximately 20°C less than the unisomerized RJ-5.

(d) Cooligomerization of cyclopentadiene and methylcyclopentadiene was accomplished by heating their commercial dimers at 190°C under autogenous pressures. Trimers corresponding to C_{18} cooligomers were isolated from the resulting mixture by vacuum distillation. Monomer and dimer decomposition products, resulting from excessive vacuum distillation conditions, have been recycled to subsequent oligomerizations to increase overall trimer yield. The isolated olefinic trimers may be readily hydrogenated over a nickel on Kieselguhr catalyst to produce saturated compounds which are precursors of alkyl diamantanes.

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ABBREVIATIONS

Reagents:

$AlCl_3$	Aluminum Chloride
CPD	Cyclopentadiene
DCPD	Cyclopentadiene endo dimer
HNN	Hydrogenated Norbornadiene endo, endo hexacyclic dimer
H_2SO_4	Sulfuric Acid
MCPD	Methylcyclopentadiene
NN	Norbornadiene endo, endo hexacyclic dimer
$NN^=$	Olefinic Norbornadiene endo, endo hexacyclic dimer
NBD	Norbornadiene
THB-S (or THBinor-S)	Tetrahydro Binor-S
THTriMeCPD	Tetrahydrotri(methylcyclopentadiene)
TriCPD	Tri(cyclopentadiene)
THTriCPD	Tetrahydrotri(cyclopentadiene)
Wt.%	Weight percent
XN	Norbornadiene exo, endo hexacyclic dimer
XX	Norbornadiene exo, exo hexacyclic dimer
NXN	endo, exo, endo
H_2	Hydrogen
KCl-HOH	A saturated solution of potassium chloride in water
HCl	Hydrogen chloride gas
Rh	Rhodium
ΦCH_3	Toluene

Analytical:

Cap GC	Gas chromatography using a high resolution capillary column
GC	Gas chromatography
HP5830A	Hewlett-Packard Model 5830A gas chromatograph
MS	Mass Spectroscopy
SD	Column chromatographic simulated distillation
VPC	Gas Chromatography or Vapor Phase Chromatography
DSC	Differential Scanning Calorimetry
TGA	Thermal Gravimetric Analysis

SECTION I

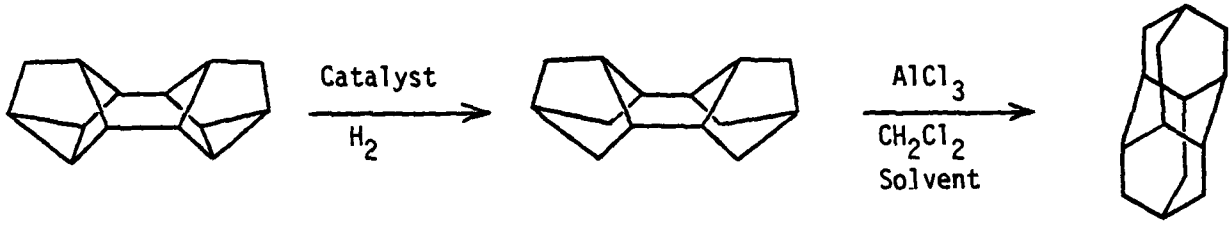
INTRODUCTION

OBJECTIVES AND BACKGROUND

A. Preparation of Diamantane - Task I

Our objectives are to develop a commercially feasible procedure for the preparation of diamantane and to produce three pounds of diamantane of greater than 97% purity by this procedure.

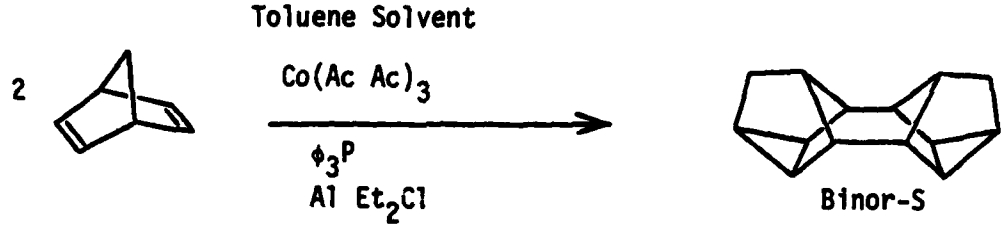
The best available procedure for preparing diamantane has been employed, i.e., hydrogenolyzing the two cyclopropane rings in heptacyclic Binor-S and isomerizing the resultant pentacyclic hydrocarbon in a solvent of methylene chloride with small amounts of aluminum chloride (1).



Binor-S	Tetrahydro Binor-S	Diamantane
$C_{14}H_{16}$	$C_{14}H_{20}$	$C_{14}H_{20}$
Mass 184.27	Mass 188.30	Mass 188.30
Seven Rings	Five Rings	Five Rings

This approach to diamantane had previously been used at Suntech for preparing small samples (2) and it appeared to be eminently suited for scale-up.

Early in 1977, a batch of well-over fifty pounds of Binor-S of greater than 95% purity was prepared under contract with the U.S. Navy (3) in a Suntech pilot-plant employing a novel, homogeneous catalyst system developed at Suntech (4) under semi-continuous operating conditions of controlled heat release. This excellent, high-yield reaction involved the double homo Diels-Adler condensation of norbornadiene catalyzed by the system cobaltic acetylacetonate-triphenyl phosphine - aluminum diethyl chloride:



At the completion of the dimerization reaction, the product was quenched with brine and the toluene solution of Binor-S distilled to recover crystalline Binor-S.

A sizeable retain of Binor-S in toluene solution from this preparation was at hand. Distillation was required to separate Binor-S from the solvent and dimerization catalyst residues. All Binor-S requirements had been met from this source so that this material was available to the program on a no-cost basis.

Hydrogenolysis of the cyclopropane rings in Binor-S has been extensively studied in the literature (1,5). Recently at Suntech, a superior hydrogenolysis catalyst consisting of 5% rhodium-on-alumina was found to open the cyclopropane ring in neat, hydrogenated endo, endo dimer of norbornadiene at 100 psi and around 170° (6). This catalyst has been selected for the hydrogenolysis of neat Binor-S.

Tetrahydro Binor-S in solution with methylene chloride, on treatment with small amounts of aluminum chloride, is rapidly and quantitatively isomerized to diamantane at ambient temperature and precipitated as crystalline raw diamantane. After quenching the entire reaction mixture with brine, the diamantane is dissolved and recrystallized from ideal solvents. This is sufficient to give diamanatane in greater than 97% purity.

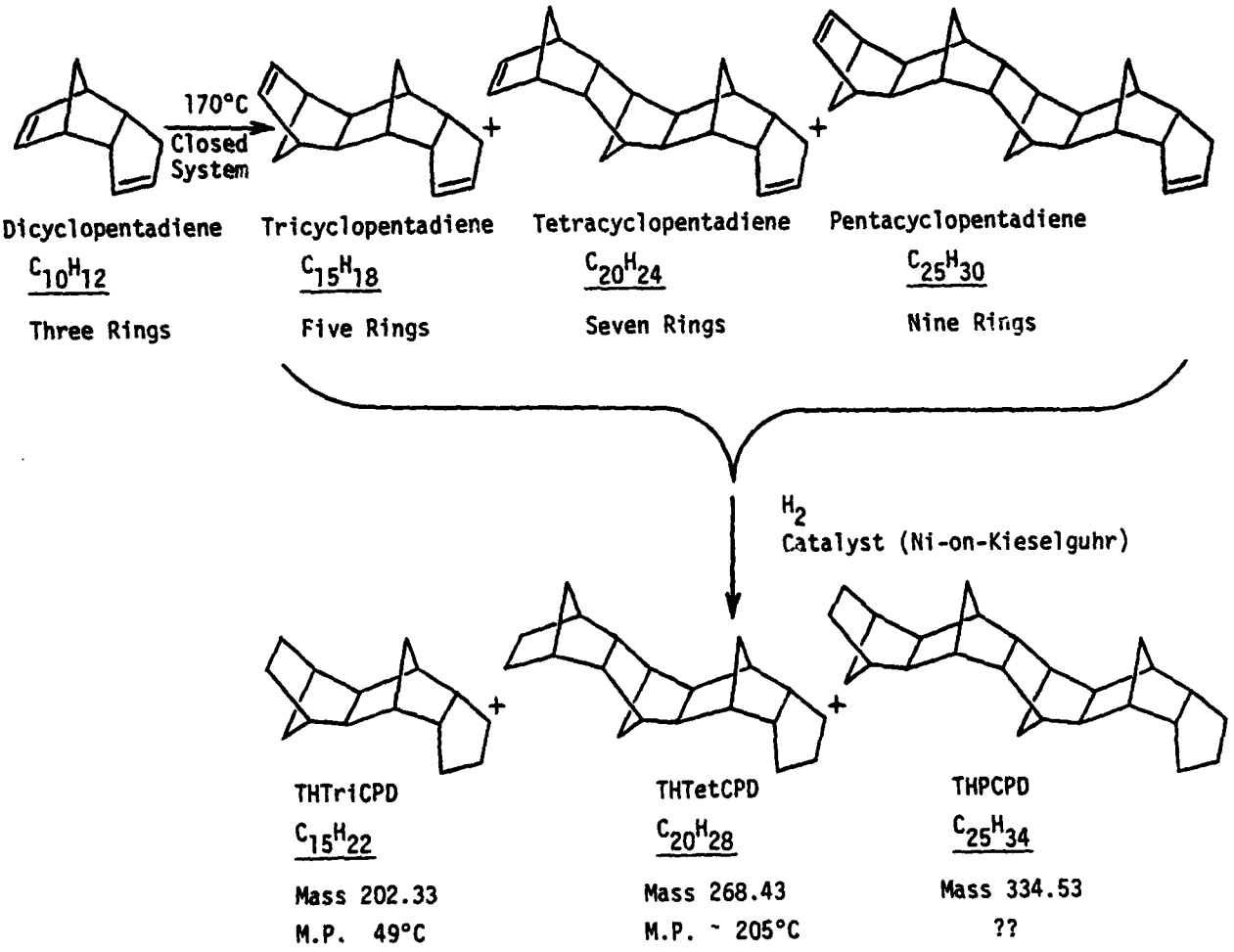
B. Preparation of exo-Tetrahydrotri(cyclopentadiene) (XTHTriCPD) - Task II

The objectives of this task were:

1. To define the conditions of maximizing the yield of crystalline endo, tri(cyclopentadiene) (TriCPD) during the cracking and condensation of dicyclopentadiene, and for isomerizing endo-THTriCPD by treatment with aluminum chloride to a non-freezing missile fuel with viscosity, density and net volumetric heat of combustion as close as possible to those of conventional RJ-5.

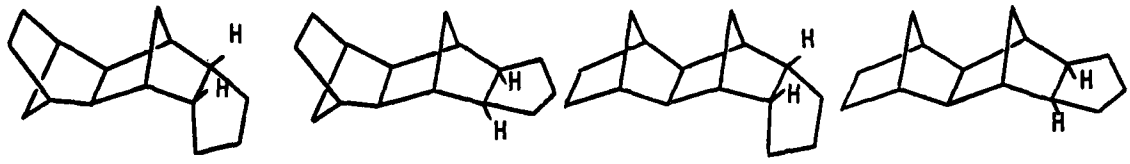
2. To prepare one quart of the optimally isomerized exo-THTriCPD and to obtain the required set of property data on this sample.

The readily available endo, exo, endo isomer of THTriCPD (MP 48.9°C (7)) is made by distilling the trimer fraction from the product of heating dicyclopentadiene in a closed system at around 170°C, followed by catalytic hydrogenation of the reaction mixture (8):



By adjusting temperature and heating time during cracking and condensing, the yield of trimer can be maximized.

Straightforward isomerization of endo-THTriCPD with aluminum chloride at 0-20°C in a solvent of methylene chloride has been shown to yield a non-freezing mixture of isomers to which have been assigned the following tentative structures (9):

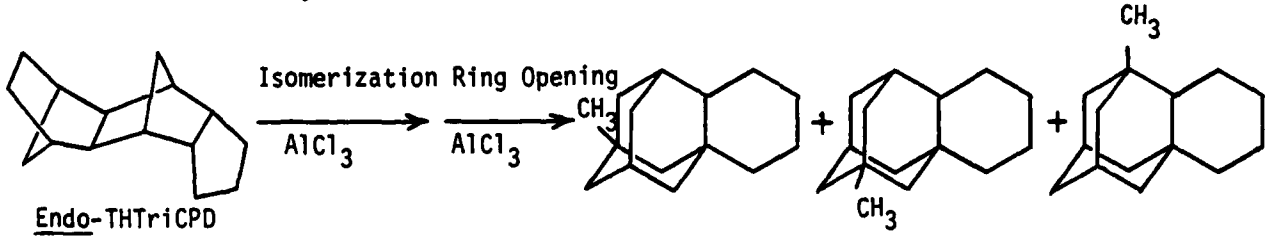


Decreasing
VPC Retention Time →

Peak #1	Peak #2	Peak #3	Peak #4
Endo-Exo-Endo	Endo-Exo-Exo	Exo-Exo-Endo	Exo-Exo-Exo
M.P. 120°F	??	??	??
Starting Material			
Structure Definite	Speculative	Speculative	Speculative

It appears that the starting material (GC Peak #1) has the highest viscosity and density of any of the isomers in the mixture. In order to minimize viscosity, Peak #1 material may be isomerized practically to extinction. Fortunately, at equilibrium at ambient temperature, the concentration of Peak #1 isomer is very small, while those of Peak #3 and #4 become predominant (10).

Isomerization of endo-THTriCPD with aluminum chloride at temperatures above ambient has been shown to induce ring-opening, probably forming condensed cycloalkyladamantanes, which further lowers both viscosity and density:



Endo-THTriCPD
$C_{15}H_{22}$
Mass 202.33
Five Rings

Methyl-1,2-Tetramethylene-Adamantanes
$C_{15}H_{24}$
Mass 204.34
Four Rings

Thus it appears that minimum ring-opening during isomerization to extinction of the starting endo-THTriCPD is required to achieve the high-energy objectives quoted above.

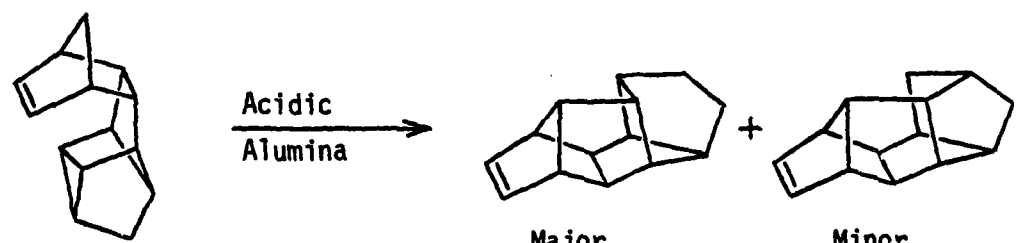
C. Preparation of Hydrogenated Product of Isomerized endo, endo-Di (Norbornadiene) - Task III

The objectives of this task were:

1. To explore fully the synthesis of the hydrogenated product of isomerized endo, endo-di(norbornadiene).

2. To prepare multi-gallon-size quantities of the optimum product.

3. To obtain pertinent property data on the optimum product. At Suntech, Inc., a procedure has been developed for completely isomerizing the endo, endo olefinic dimer concentrate by slurrying and heating this material with acidic alumina (11). Two preponderant product compounds, isomeric with the endo-endo olefinic dimer, are formed with loss of the cyclopropane ring, but with the simultaneous formation of an additional ring. The assumed structures of these isomers are:



$C_{14}H_{16}$
Six Rings

Major
$C_{14}H_{16}$
Six Rings

Minor
$C_{14}H_{16}$
Six Rings

By varying reaction temperatures between 170°-230°C and by varying the acidic alumina catalyst used, one can adjust the ratios of these major and minor isomers. Also, as the conversion of starting material reaches 90%, small amounts of the olefinic dimer begin to form tetramer material which is dense but viscous; the presence of which drastically raises the viscosity of the isomerized product at ambient temperatures. If desired, isomerized dimer may be separated from tetramer by vacuum distillation. Hydrogenation of the isomerized, olefinic product is rapid and complete with nickel-on-Kieselguhr catalyst at hydrogen pressures of 100 psig and temperatures of 100-130°C. The hydrogenated, isomerized dimers constitute a valuable, new blending agent for reducing the freezing points of conventional RJ-5 or RJ-6 fuels.

D. Preparation of Polyalkyldiamantanes - Task IV

The objectives of this task were:

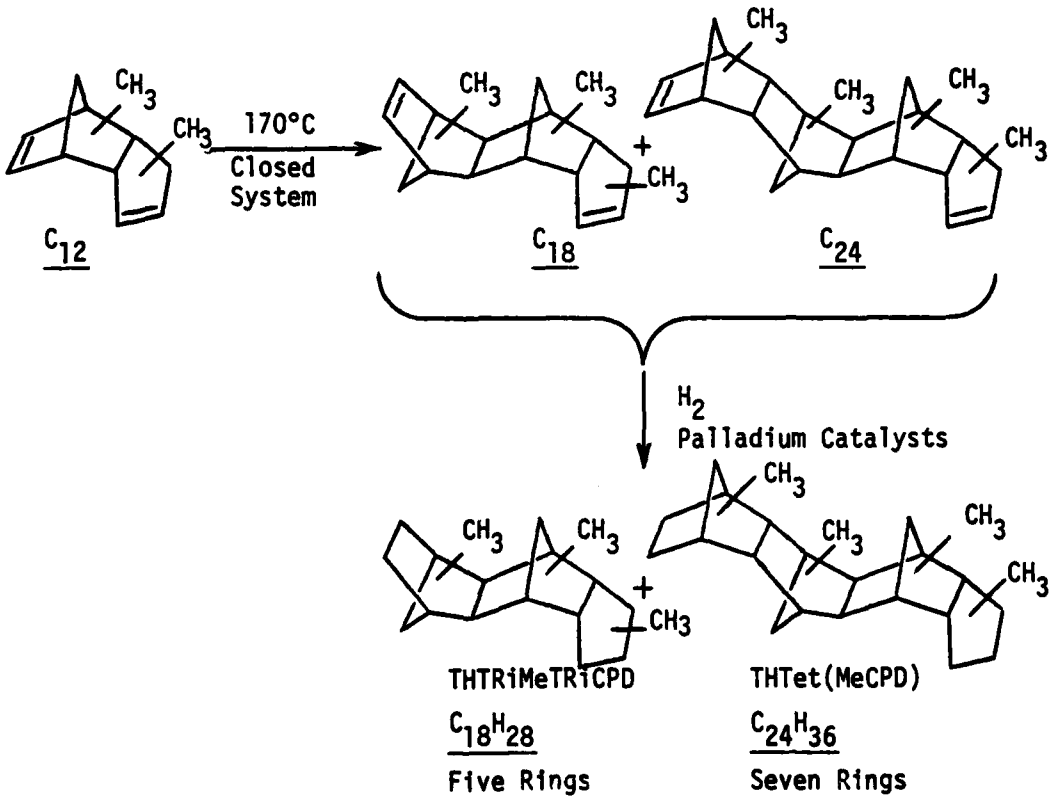
1. To convert the readily-available mixture of C_{18} THTri(MeCPD) s by isomerization into a mixture of C_{18} tri-and tetrasubstituted polyalkyldiamantanes of complexity sufficient to preclude crystallization at -65°F.

2. To prepare at least one quart of optimum product.

3. To obtain proof that polyalkyldiamantanes constitute the bulk of the product of isomerization.

4. To obtain a pertinent set of property data on the optimum product, as well as on starting material.

The homogeneous C_{18} mixture of THTri(MeCPD) s is a readily-available liquid made by heating commercial methylcyclopentadiene dimer in a sealed reaction vessel at around 170°C under autogeneous pressure. Without removing the product from the reaction vessel, the product has been hydrogenated in place at around 100 psig of hydrogen pressure by using palladium-on-carbon or palladium-on-alumina catalysts. After complete saturation of the olefinic material, it is filtered to remove catalyst, and distilled to separate trimer from dimer, tetramer and pentamer:



SECTION II

EXPERIMENTAL DETAILS AND RESULTS

A. Preparation of Diamantane - Task I

1. Binor-S Precursor Purification

A quantity of Binor-S had been previously prepared at Suntech in a semi-continuous dimerization of norbornadiene under Navy Contract No. N60530-77-C-0021. From this quantity a portion was used as the charge stock for preparing diamantane. In a single distillation at atmospheric pressure, through a Sarnia Mark II Fractionating column (70mm x 36", Podbielniak Helipak Packing), 29.4 lbs. of crude Binor-S were fractionated into 20 cuts as shown in Chart 1. With the exception of cuts 1 to 3, all fractions were colorless in the molten state and became essentially completely crystalline at ambient temperature. The distillation showed that Binor-S boils at 514°F (267.8°C) and has a specific gravity of 1.1310 at 60°F (15.56°C).

2. Binor-S Hydrogenolysis with Pd/C

A portion of cut #13 (545.3 oz., 2.96 moles) of the above mentioned fractional distillation (cf Chart 1) was hydrogenolyzed in a stirred one liter Hastelloy "B" reactor employing 34 g. of 10% Pd-on-carbon catalyst. As shown by the VPC scan of distillate Cut #13, Figure #1, this starting material was 97 wt.% pure. Three samples were taken during this hydrogenolysis to follow H_2 absorption. Samples #1 to #3 were liquid at ambient temperature. Figures 2, 3 and 4 are ordinary analytical vapor phase chromatograms (using a HP5830A instrument) and charts 2, 3 and 4 are mass spectrograms of samples #1, 2 and 3 respectively. In Figure 2 the peaks with retention times of 35.15 and 36.18 minutes correspond to the hexa- and penta-cyclic products of one and two cyclopropane ring-openings per Binor-S molecule and each of these peaks may be composed of two isomers.

Sample #1, a relatively mobile liquid at ambient temperature, did not crystallize after three weeks of storage as a glass at dry ice temperatures. Sample #3 did crystallize within one week of storage under these conditions. The density of sample #3 was 1.0658 @ 20°/4°, its viscosity at 100°F was 14.51 cs and its net heat of combustion was 159,389 btu/gal.

3. Binor-S Hydrogenolysis with Rhodium

Four "large-scale" reactions were made with rhodium catalyst to prepare sufficient tetrahydro Binor-S for synthesizing the three pounds of diamantane called for in Task 1 of this contract. The catalyst support was varied and the amount of catalyst necessary to achieve the complete hydrogenolysis of the Binor-S' two cyclopropane rings in a "reasonable" time interval was minimized.

With the first two reactions a 5% Rhodium on alumina catalyst was employed and in the third and fourth reactions . . . a 5% rhodium on carbon.

Typical of these reactions was run #HKM 7/26/78 (1). Here, 7.0g (1.0 wt.% of Binor-S) of a 5% rhodium on carbon (Engelhard) catalyst was charged to 700g of molten (70°C), 97% pure (3.7M) Binor-S in a one liter Hastelloy "B" batch type reactor. The reactor was sealed and all air displaced by bubbling argon through the liquid Binor-S. Then the argon was displaced by hydrogen gas (H_2). Reactor contents were warmed to a maximum of 249°C while stirring at 1200 rpm and the gas pressure was controlled at a maximum of 430 psig. While warming, the reactor was initially sealed-off from the H_2 reservoir until hydrogen absorption began. Hydrogenolysis began at 204° and 390 psig, which was 50 min. after beginning reactor heating and stirring; it was rapid and without mishap.

Samples of reactor contents were taken at 150 min., 170 min., and 190 min. after introducing heat to the reactor. Sampling required a slight loss of H_2 since the sample line was coincident with the H_2 inlet line. Heating and stirring were discontinued 7.5 hours after applying initial heat. Then after slowly cooling overnight (16 hours), the reactor liquid contents were filtered, producing a crystal clear liquid product weighing 675g.

The following tabulation (Table 1) lists the conditions existing during the formation of each sample from HKM 7/26/78 (1).

TABLE 1

Binor-S Hydrogenolysis with Rh

7-26 (1) Sample #	Time for T° During Reaction Minutes	T° Range (°C)	Reactor P During Reaction (PSIG)	ΔP of H_2 Reservoir (PSIG)	Absorbed H_2 (Moles)	Required H_2 (Moles)	Binor-S Charge (Moles)
1	100	204-245	390-410	1770-1500 = 270	10.5-8.9 = 1.6	7.6	3.8
2	20	240-249	400	1500-1190 = 310	8.9-7.1 = 1.8		
3	20	245-249	400	1190- 900 = 290	7.1-5.3 = 1.8		
Final	260	225-249	400-419	900- 495 = 405	5.3-2.9 = 2.4 / 7.6		

VPC Analyses of these samples are included with this report as Figures 5, 6, 7 and 8.

4. Purification of Tetrahydro Binor-S with H_2SO_4

In purifying the THB-S, emphasis was placed upon removing trace amounts of compounds still retaining an unhydrogenolyzed cyclopropane ring.

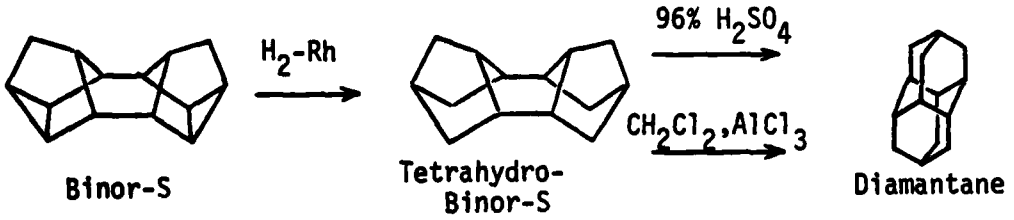
To accomplish this task, one part of THB-S was lightly shaken for approximately two minutes with between 1 and 2 parts of 96% sulfuric acid. After settling into two liquid phases, the supernatant upper layer was filtered through "Celite" diatomaceous earth, producing a crystal clear liquid; the spent, dark-russet sulfuric acid lower layer was discarded. The purification resulted in a THB-S loss of 5.2 to 9.1 wt.%.

This purification technique was used with many THB-S isomerization charge stocks but most isomerizations to diamantane were carried out successfully upon neat, untreated, "unpurified" THB-S. Yields are recorded in Table 2.

5. Tetrahydro Binor-S Isomerization to Diamantane

a. Sulfuric Acid Catalyst

A few exploratory qualitative reactions were investigated using concentrated (96%) sulfuric acid as catalyst to isomerize THB-S to diamantane.



One simple technique consisted of shaking 2.0 ml of hydrogenolyzed Binor-S with .75 ml of concentrated sulfuric acid in a glass bottle under argon at ambient temperatures. Shaking continued for two hours with the formation of very little crystalline product (HKM 7/12/78(1)). In a second reaction (HKM 7/13/78(1)), 20 ml of sulfuric acid was shaken 16 hours at ambient temperatures with 6 ml of hydrogenolyzed Binor-S. Upon settling, two liquid phases separated: a lower russet acid layer and a crystal clear upper layer which contained solid peach-colored crystals. These crystals were washed with water, then with chilled dichloromethane until they were white. They were then dissolved in n-pentane and analyzed via VPC. Said scan, showing unidentified multiple products, is displayed as Figure 9.

b. Aluminum Chloride Catalyst

Tetrahydro Binor-S was successfully isomerized to diamantane with the Friedel-Crafts catalyst, Aluminum Chloride. Seven batch reactions and four continuous reactions were performed upon both H_2SO_4-scrubbed and neat THB-S.

In the continuous reactions, the reacting slurry was "pumped" by refluxing solvent into a thimble within a Soxhlet extractor atop the reaction flask. The thimble strained solid diamantane from the slurry and returned unisomerized THB-S and solvent to the reaction flask.

One batch isomerization was HKM 9/29/78(1). Here, 600g of neat THB-S, not scrubbed with H_2SO_4, was stirred, under an Argon atmosphere in a one liter erlenmeyer flask equipped with a condenser, with 200g of aluminum chloride (an excess $AlCl_3$ was used to test this catalyst parameter), in 300 ml of refluxing (40°-65°C) dichloromethane at atmospheric pressure for 5.67 hours. The reacting slurry gradually became dark brown in color as isomerization of THB-S progressed. Crystals developed which floated upon the surface of the reactor liquid. There was no excessive exotherm. After discontinuing stirring and heating and allowing the $AlCl_3$ to settle 1/2 hour, the reactor supernatant was decanted through a Whatman #1 qualitative paper filter, leaving in the flask the undissolved $AlCl_3$ - on to which the filtered supernatant was redeposited in order to increase diamantane yield. Then the filter cake of diamantane was washed sequentially with 900 ml of chilled (10°C) dichloromethane, one liter of water and 600 ml of methanol. This resulting first crop of tan colored "raw" diamantane weighed 42.15g, still damp with methanol. All of the filtered supernatant was stirred with the remaining $AlCl_3$ an additional 64 hours at ambient temperatures. This recycled filtrate was then also allowed to settle 1/2 hour and the supernatant filtered. The filter cake was washed with 400 ml of water and then 400 ml of methanol, and yielded an additional 60 g of methanol-damp "raw" diamantane. Total yield of dry "raw" diamantane from this reaction was 447.9 g or a yield of 74.65%. There remained in the flask an estimated 85-110 g of undissolved $AlCl_3$.

Table 3 summarizes additional reactions of THB-S to diamantane.

6. Diamantane Purification

Seven separate runs were performed to purify > 3 pounds of diamantane by recrystallization. Pentane, Hexane and Toluene (ϕCH_3) solvents were investigated.

A typical example of the technique used is HKM 10-2-78(1). Here, 392.1 g of dichloromethane-damp, "raw" diamantane from HKM 9-29-78(1) was mixed at 24°C with 1500 ml of ϕCH_3, and the mixture stirred and heated to induce ϕCH_3 reflux. Heating was continued for 2 hours to produce a ϕCH_3 solution. This 2 liter ϕCH_3-diamantane mother liquor was filtered hot through a coarse fritted glass filter funnel and the filtrate heated under an argon stream so as to evaporate ϕCH_3, thereby condensing the volume to 1 liter. This concentrated supernatant was allowed to cool slowly in 21°C ambient surroundings for 16 hours. Large white crystals of diamantane developed. The beaker and contents were then further cooled for 15 minutes in wet ice, and the diamantane crystals filtered from the supernatant through a coarse fritted glass filter funnel. Diamantane as a filter cake was subsequentially washed with 500 ml of ~10°C ϕCH_3 and 500 ml of ~20°C methanol. This initial "crop" of diamantane was dried in air at 110°C to produce 237.3 g of >97% pure product. Methanol and toluene washes were not mixed. The supernatant filtrate plus the toluene wash from the first recrystallization was further condensed to 750 ml and this mother liquor was cooled by wet ice and filtered, as the first "crop", to produce a second "crop" of 12.7 g of pure diamantane.

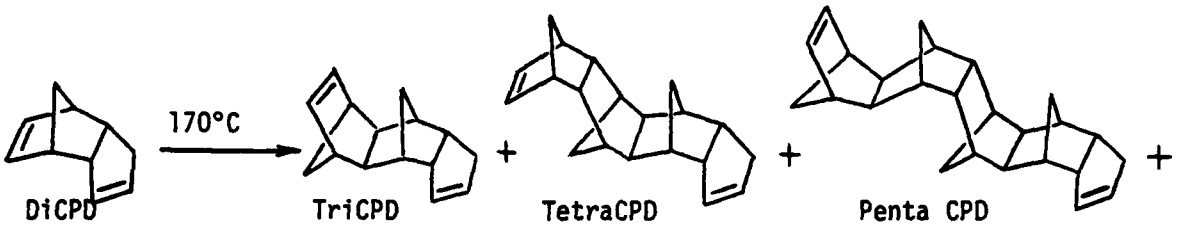
The final three pound sample of >97% pure diamantane exhibited a melting point of 245°C by the Hoover "Uni-melt Capillary Melting Point Apparatus" and a sample evaporated completely at 255°C without leaving a residue in a Thermal Gravimetric Analyzer.

An encapsulated example of our finalized process for synthesizing Diamantane from Binor-S is depicted in Table 4.and Table 9 describes physical properties.

B. Preparation of Exo-tetrahydrotri(cyclopentadiene) - Task II

1. Cyclopentadiene oligomerization

In the task of preparing multi-gallon quantities of endo-tetrahydro tri(cyclopentadiene), five batches of cyclopentadiene dimer were thermally treated in a one gallon stirred reactor.



Reaction times of 7 and 10 hours and temperatures ranging between 170° and 200°C were used to produce mixtures of tri, tetra and penta-cyclopentadiene.

Table 5 summarizes CPD oligomerizations. A typical simulated distillation analysis of these oligomerizations (EJJ-743117) is included as Figure 10 and Chart #5.

2. Isolation of Cyclopentadiene Trimers

Attempts to separate the CPD oligomeric mixture into its respective oligomers by varying heat gradients, ultrasonic treatments, and 2-propanol and n-hexane extraction proved futile. Vacuum distillation produced the only pure sample of CPD trimers.

A small scale scouting distillation was performed at 0.05 to 0.09 mm Hg pressure using a magnetic stirring system and heating with an oil bath. Two distillation cuts were taken from a 132 g charge. The initial cut boiled at 28 - 40°C and .07 mm Hg pressure; it was mainly dicyclopentadiene (DCPD) and was 20% of the charged mixture. A second cut boiled at 92 - 97°C and 0.05 - 0.09 mm Hg pressure; it was mainly Tri CPD isomers and made up 39% of the charged mixture.

Two larger distillations of CPD oligomeric mixtures were performed to isolate the necessary quantity of trimer for contract requirements. These scale-up fractionations used an electrical heating mantle to supply heat to the still pot.

One run (HKM 10/13/78(1)V) charged 2780.9 g of mixture and isolated 1000 g of CPD trimer, thus distilling all but 842.9 g of residual oligomers from the pot. This residue was sent to Mr. G. W. Burdette, Naval Weapons Center, China Lake, California, to be considered as a high energy hydrocarbon fuel candidate for ramjets and rockets.

In the second large scale distillation (HKM 11/9/78(1)), 5329.9 g of CPD oligomeric mixture was charged, and ~1600 g of CPD trimer was extracted when evidence appeared of decomposition of the oligomers still remaining in the pot. CPD began to appear in the distillation receiver and the distillation was discontinued. Charts 6 and 7 summarize the distillation data and properties of components from these two large scale runs.

3. Hydrogenation of Cyclopentadiene Trimers

To saturate the isolated TriCPD, 629 g was charged to a stirred Hastelloy "B" autoclave with 50 g (8%) of 60% nickel on Kieselguhr catalyst (Harshaw Ni-0104)). This mixture was stirred for fourteen hours while heating. The highest temperature throughout the run was 147°C under a hydrogen pressure of 111-162 psig. The hydrogen reservoir pressure drop indicated 98% saturation after six hours of stirring. Olefinic saturation of samples was verified with mass spectroscopy and gas chromatography analytical techniques. Upon cooling to 30°C the reactor contents were filtered through a Whatman #1 qualitative filter paper, thereby removing the nickel catalyst and producing 542 g of a crystal clear liquid -- which, upon standing at ambient temperatures, solidified to a white waxy substance. With a Hoover Uni-melt capillary melting point apparatus the melting point of this final tetrahydrotri(cyclopentadiene) was estimated to be 26°C.

4. Isomerization of Cyclopentadiene Trimer

a. Using Acidic Alumina

One tangential scouting experiment was performed to assay possible merits of using acidic alumina rather than $AlCl_3$ to isomerise CPD trimers. Here in HKM 10/17/78(1), 2 ml of neat tri(cyclopentadiene) from HKM 10/13/78 Cut #12 was heated for 8.2 hours with 0.2 g of acidic alumina (Harshaw Al 1605P). During this time the mixture temperature ranged from 168° to 204°C. High resolution capillary gas chromatographic scans as Figures 11, 12 and 13 show that some conversion did result.

b. Using Aluminum Chloride ($AlCl_3$)

A typical isomerization of the saturated cyclopentadiene trimers was reaction HKM 11/29/79(1) where 200 g of THTriCPD was mixed with 256 g of dichloromethane at 30°C in a one liter three-necked Morton flask equipped with an overhead stirrer. The mixture was cooled to -10°C; 30 g of $AlCl_3$ was added; the liquid was saturated with hydrogen chloride gas for eight minutes by bubbling said gas into the liquid, and, while stirring the resulting mixture for 2.67 hours, the temperature was kept below 14°C with a cooling bath. Next, the supernatant was siphoned from the settled $AlCl_3$ through a coarse fritted disc filter funnel. Dichloromethane solvent was stripped away from the filtered supernatant while gradually raising the temperature to 99°C. Then aspirator vacuum was applied to remove traces of solvent. Invariably, two liquid phases separated upon removing solvent -- an upper oil product layer and a lower red sludge layer. The supernatant oil was decanted from the sludge, scrubbed with an equal volume of a saturated potassium chloride-water solution (note: in a subsequent run, HKM 1/4/79(1), this decanted oil was filtered through diatomaceous earth before washing it with potassium chloride solution) and then filtered through a Whatman #1 qualitative paper and diatomaceous earth (Celite) to produce 144 g of a clear faintly yellow liquid that remained fluid at 0°C.

Monitoring gas chromatographic scans of HKM 11/29/78(1) including charge and final isomerized product, are included as Figures 14, 15 and 16.

In reaction HKM 11/30/78(1), where fresh THTriCPD and $AlCl_3$ were added to spent $AlCl_3$ catalyst from a previous reaction, (HKM 11/29/78 (1)) no interference was readily discernable.

A mass spectrographic scan of the residual isomerized THTriCPD that had sat with $AlCl_3$ overnight is included as Chart 8 and a mass spectrographic scan of the final isomerized product from HKM 11/30/78(1) is included as Chart 9.

High resolution gas chromatographic scans and mass spectrographs of other isomerization reaction products are depicted as Figures 17 and 18, and Charts 10 and 11.

5. Purification of Isomerized Tetrahydrotri(cyclopentadiene)

Purification of the final isomerized CPD trimers was achieved by both clay percolation and vacuum distillation.

One particular distillation, HKM 12/14/78(1), was performed without previously clay treating the raw isomerized THTriCPD. To this distillation pot was charged 1041 g of raw isomerized CPD trimers. Cut #1 withdrew a 29.2 g precut with 9.8 g escaping to a dry ice trap; there was an 823.3 g middle-cut trimer in two portions as Cut #2 boiling @ 81°C - 108°C at .04 - .09 mm Hg and finally 28.5 g as Cut #3 -- leaving a 139.5 g residue. The first portion of Cut #2 (455 g) still contained trace dimer and was therefore redistilled. Cuts #2 and #3 were combined producing ~826 g of trimers.

These were then percolated through 75 cc of serpentine clay (Florisil) which clay discolored substantially.

Another trimer cut (162 g), HKM 1/9/79(1) from HKM 1/4/79(1) isomerization was also percolated through serpentine clay (100 cc or 47 g) without discoloring the clay.

As has been cited and as will be mentioned again in the following discussion, this trimer from HKM 1/4/79(1) was percolated through diatomaceous earth before scrubbing it with potassium chloride solution. The final composite sample of isomerized tetrahydrotri(cyclopentadiene) was percolated through serpentine clay as a final purification.

Table 6 summarizes quantitative examples of isomerized THTriCPD production, and Figure 19 verifies the absence of significant polymers by showing that all but 2.6% of a sample of isomerized THTriCPD evaporates at 270°C under a nitrogen stream.

Table 9 presents isomerized THTriCPD physical properties.

C. Preparation of Hydrogenated Product of Isomerized endo, endo-Di(Norbornadiene) - Task III

1. Olefin Purification

Purification of the bright yellow olefinic endo, endo norbornadiene hexacyclic dimer ($NN^{=}$) of traces of catalyst residues presented more of a problem than the saturated analog (HNN) since the olefin reacted violently with activated acidic filtrol clay, and also since it tended to desorb impurities in percolation treatments.

When contacting the olefinic dimer, $NN^{=}$, with 7.5 wt.% of superfiltrol clay which had been dried for two hours at 100°C, a violent exotherm occurred. This created dark color bodies and resins which remained absorbed on the clay, and did not remove the yellow discoloration from the starting olefin. Next, this same batch of olefinic dimer was contacted overnight with a 90/100 mixture of unactivated Attapulgus and super filtrol clays. No exotherm was evident but no apparent reduction of the yellow color was found on filtering the clay from the liquid.

This batch of dimer was then percolated through 14.8 wt% of basic alumina which had been dried one hour at 100°C. Again no decrease in color was apparent. With the same aliquot of dimer, percolation through 38.6 wt.% silica gel (dried one hour at 147°C) was then tried with no improvement evident. Finally, the same batch of olefin was percolated through 21.8 wt.% of 100-200 mesh Florisil (Fisher F-101, Lot 735726 magnesium silicate) in a 4.4 cm diameter glass column. The Florisil had previously been activated by heating for 1/2 hour at 145°C. The olefin effluent showed a marked reduction in color.

2. Isomerization of Olefin

On stirring and heating a suspension of 10 wt.% of acid-washed alumina (Merck #71695 or Harshaw Al-1605P) in the $NN^{=}$ concentrate which had been almost completely rid of traces of catalyst by percolation through Florisil, no reaction was found by VPC monitoring until the temperature reached around 160°C. At 170-190°C there began a moderately rapid formation of a complex mixture of isomers having shorter Chromatographic retention times than the starting material, and an orderly decrease in concentration of charge persisted until the complete conversion of this starting material. This was monitored by a Hewlet-Packard 5830A gas chromatograph as exemplified in figures 20-25.

During the reaction the Alumina developed a light orange color

and the liquid became light yellow. Little conversion to low molecular weight products of cracking took place. Thermal gravimetric analysis indicated that all but 2 wt.% of one liquid product evaporated under a stream of nitrogen at 270°C. (Figure 26). At high conversions of the NN dimer the viscosity of the product of isomerization was somewhat higher than that of the starting material. Mass analysis of a sample of the hydrogenated product shows an amount of tetramer with the expected mass of 370. VPC analysis of the olefinic product indicated an array of at least five peaks, the formation of two low-boiling peaks in preponderance, and essentially the complete disappearance of the starting olefin.

This isomerization was scaled up in an experiment in which the purified olefinic NN dimer under argon was treated with 10 wt.% (of olefin) of acid-washed alumina (Merck #71695); the temperature was gradually raised to a maximum of 180°C and the experiment terminated after a total contact time of 19.8 hours. The final olefinic product, containing less than 8% of the starting NN olefinic dimer, had a density of 1.1237.

3. Hydrogenation of Isomerized Olefin

The isomerized olefinic mixture was completely and rapidly hydrogenated using 10 wt.% nickel-on-kieselguhr catalyst (Harshaw Ni-0104P) at 100 psig of hydrogen and a maximum temperature of 113°C over a period of two hours. Filtration produced a clear, pale yellow (~24 Saybolt) liquid which formed a glass but did not crystallize on three day storage at -78°C. This material's density was 1.1097 and the net heat of combustion 163,000 BTU/gallon. Infrared analysis disclosed the absence of cyclopropane rings, but mass analysis indicated that hexacyclic material with a mass of 186 was the major constituent of the product. Mass analysis also showed that a minor amount of tetramer ($C_{28}H_{34}$, mass 370) had formed in approximately the ratio of 100 parts of dimer to 15 of tetramer. This tetramer may explain why thermo-gravimetric analyses of the hydrogenated, rearranged products show higher contents of residual material than HNN dimer; for example, one isomerization tested 13.5 wt.% residue remaining at 270°C.

4. Purification of Hydrogenated Isomerized NN

Final isomerized saturated endo, endo hexacyclic dimer may be purified by standard distillation or by percolating or contacting it with adsorbant clays.

Distillation may be performed at atmospheric or reduced pressures and such procedures are well known to those in the art. Clay treatment may be performed by percolating the final liquid

through a bed of, preferably neutral pH, adsorbants at ambient or lower temperatures or by batchwise stirring the final liquid with such adsorbants.

In one contact treatment, HKM 4/20/78(1), 581.8 g of faintly yellow saturated isomerized NN stirred under a hydrogen blanket for two hours at 22°C with a mixture of clays consisting of: 19.6 g acid bentonite (Superfiltrol), 18 g silica gel, 18 g Attapulgus, and 18 g of serpentine clay (Florisil). After settling 6 hours the supernatant was filtered through a Whatman #1 quantitative paper to produce a crystal clear liquid.

Physical properties of the final product are depicted in Table 9.

D. Isomerization of C_{18} Tetrahydrotri(Methylcyclopentadiene)s - Task IV, A

1. Cooligomerization of Cyclopentadiene and Methylcyclopentadiene (MCPD)

Quantities of cyclopentadiene-methylcyclopentadiene cooligomers were produced by heating various molar ratios of CPD and MCPD dimers for approximately thirty hours in a batch-type, stirred, one gallon Hastelloy "B" autoclave. Products of different consistencies resulted. Simulated distillations showing varied selectivities are included as Figures 27-30. To determine whether high molecular weight polymers and resins were produced, Thermal Gravimetric Analyses were made of final products. Figure 31 illustrates the evaporation rate, under a nitrogen gas stream, of these cooligomers to less than 3% resin at 350°C. Table 7 summarizes conditions and results of four such cooligomerizations.

2. Isolation of CPD-MCPD Trimers

Cooligomers from HKM 3/9/79(1) were fractionated using heat and vacuum so as to isolate the trimers of cyclopentadiene - methylcyclopentadiene. This distillation progressed well, separating monomers and dimers from trimers, but then as the trimers diminished from the distillation pot, and as the pot liquid temperature exceeded 162°C at 0.05 mm Hg pressure, chemical "cracking" began in the pot, forming different compounds. A pure trimer fraction was successfully isolated, claiming 94% of that available according to simulated distillation analysis. This is shown by the included SD scan of HKM 3/9/79(1) Cut #4, Figure 32. However, in attempting to fractionate the higher boiling tetramers, decomposition produced lower boiling monomers and co dimers as indicated in the enclosed gas chromatographic scan of distillation Cut #7, Figure 33.

SECTION III

DISCUSSION OF EXPERIMENTAL RESULTS

A. Preparation of Diamantane - Task I

Starting with excess Binor-S from a previous U.S. Navy contract facilitated this diamantane preparation. Said Binor-S was easily purified by distillation and readily hydrogenolyzed by a Suntech process using a rhodium heterogeneous catalyst. Since two moles of hydrogen were required for each mole of Binor-S used in this hydrogenolysis, 7.6 moles (15.2 g) of hydrogen were expected to be absorbed in reaction, HKM 7-26-78(1). From 1770 psig (10.5 moles) of hydrogen initially in our 2.1 liter hydrogen reservoir, the pressure, as the reaction was terminated, had decreased to 495 psig (2.9 moles) of hydrogen, exactly 7.6 moles absorption. This insinuates the complete hydrogenolysis of the Binor-S'cyclopropane rings.

Steps were taken to eliminate any partially hydrogenolyzed Binor-S (Mass 186) from some reactions by scrubbing hydrogenolyzed product with sulfuric acid, but this extra step produced no observable advantage to the process.

Sulfuric acid catalysis was also investigated as an avenue to diamantane from tetrahydro Binor-S. This isomerization proceeded slowly but produced only trace positive results after shaking with THB-S overnight. VPC analysis indicated one 70% isomer, probably diamantane, and another 22% isomer, possibly partially rearranged THB-S. Further investigation was not deemed efficient time-usage in light of the slow conversion rate.

The aluminum-chloride-catalyzed tetrahydro Binor-S isomerization to diamantane proved to be the best method available from "stated chemical art". When constructing a process based upon the enclosed experimental data, one should consider that solvent filtered from this isomerization (HKM 8-7-78(1)) may be recycled to subsequent reactions. It is also to be emphasized that these isomerizations may be performed in a continuous reactor. In one reaction (HKM 8-10-78(1)), the $AlCl_3$ catalyst was increased to 35 wt. % of charged THB-S but 17.5 wt. % $AlCl_3$ performed as well.

Purification of the "raw" diamantane was begun using solvents having precedence in chemical literature. Other investigators have successfully recrystallized diamantane from methylene chloride and n-pentane (1).

Our experience with these solvents indicates that they may create a volume problem in a commercial process, since approximately 1500 ml of refluxing methylene chloride was required to dissolve 100 g of "raw" diamantane in a reasonable time.

We then went on to recrystallize diamantane from n-hexane. One could heat the solvent-solid slurry to 68°C and achieve better solubility of the "raw" diamantane (100 g diamantane/liter $n\text{-}C_6$) in a reasonable time, but the quantity of solvent was still regarded as excessive for a commercial process.

Finally, toluene was tried as a diamantane solvent. Here, only 382 ml of refluxing solvent (111°C) was necessary to dissolve 100 g of "raw" diamantane.

In attempting to determine the melting point of our purified diamantane by DSC, at least three distinct endothermic peaks were produced rather than one peak (Figure 34). Literature investigations revealed that as some crystals are warmed, a rearrangement of crystal structure becomes possible and this rearrangement absorbs heat - momentarily halting the sample temperature increase - which then produces a DSC peak similar to a melting-point peak (12).

B. Preparation of exo-Tetrahydrotri(cyclopentadiene) - Task II

The first step in producing THTriCPD, thermal oligomerization of CPD, was straightforward and convenient. Isolating the sensitive trimer oligomer, however, required certain precautions.

When vacuum-distilling heat-labile diolefins, such as tricyclopentadiene, it is imperative that the distillation pot charge be heated uniformly and that the quantity of oligomer mixture is small enough to allow adequate heat transfer. Electrical heating mantles often contain areas which exhibit non-uniform electrical resistance or non-uniform electrical wire insulation, therefore, creating "hot spots". These "hot spots" supply uneven heating to the distillation pot surface. As the distillation pot liquid thickens with higher molecular-weight oligomers, since lighter compounds are distilled out, thermal homogeneity is more difficult to maintain. Because of this, our scouting distillations made use of a pot-liquid stirrer and uniformly-heating silicone oil baths with excellent fractionation success.

Hydrogenating the isolated trimer diolefin was straightforward using the commercial, economical, heterogeneous nickel on kieselguhr catalyst. Hydrogenation was performed after isolating the diolefin so that the olefin dimer might be recycled in subsequent oligomerizations to form more trimer.

Isomerization of CPD trimers takes place heterogeneously on acidic alumina or aluminum chloride. Alumina is less expensive and an easier-to-handle catalyst but so much slower than $AlCl_3$ that we followed project proposal plans and used $AlCl_3$ to prepare the required one-quart sample.

Commercial batch reaction processes should function well, allowing spent catalyst sludge to accumulate in the reactor. When charging fresh THTriCPD and $AlCl_3$ (HKM 11-30-78(1)) to spent catalyst (from HKM 11-29-78(1)), there appeared to be no contamination interference.

Percolating decanted, isomerized THTriCPD through diatomaceous earth before scrubbing it with KCl-HOH solution seemed to eliminate discoloring distillables that may become freed by scrubbing unpercolated, decanted THTriCPD. HKM 12-14-78(1) final trimer-cut discolored serpentine clay, but HKM 1-4-79(1) isomerized trimer was percolated through diatomaceous earth before scrubbing with KCl-HOH solution and the resulting trimers did not discolor serpentine clay.

Depending upon the specifications for the final isomerized THTriCPD, purification can be achieved by distilling a heart-cut of the "raw" mixture of THTriCPD isomers or by percolating the "raw" mixture through adsorbent clays.

C. Preparation of Hydrogenated Product of Isomerized endo, endo-Di (Norbornadiene) - Task III

Alumina isomerization of $NN^{=}$ is a facile reaction. Excess charge stock contaminants may be removed with serpentine clays. In properly cleaned $NN^{=}$ concentrate, catalyst deactivation was not a serious problem and the measurement of the kinetics of this reaction as a function of temperature and catalyst concentration should be straightforward. Temperatures may be lowered and again raised to 180°C during isomerizations without product detriment.

In one isomerization, the amount of tetramer formed was indicated to be a function of conversion of starting material by simulated distillation, as shown in Table 8.

TABLE 8

$NN^{=}$ Isomerization with Alumina at 180°C

Total Reaction Time Minutes	Conversion of $NN^{=}$	% NBD Tetramer
180	10.0	2.1
545	59.3	5.9
965	80.4	6.2

After hydrogenating the isomerized $NN^{=}$, using economical nickel on kieselguhr catalyst, it may be purified either with adsorbant clays or by distillation.

It is to be noted that distillation removes NBD tetramers which aid in lowering melting points, increase heat of combustions, but also increase viscosity. If one decides to retain these tetramers and purify the final fuel by percolating it through adsorbant clays, then care should be exercised so as to control the temperature of the clay-bed since high temperatures, in conjunction with acidic clays, may initiate undesirable isomerization of even saturated compounds, especially any HNN present, and also further oligomerization.

This process has recently been successfully scaled-up in Suntech's pilot-plant facility to produce ~400 gallons of isomerized saturated endo, endo hexacyclic norbornadiene dimer for U.S. Air Force designees. (Modification P00004 of Contract No. F33615-78-C-2037).

D. Isomerization of C_{18} Tetrahydrotri(Methylcyclopentadiene) - Task IV-A

Oligomerization of CPD-MCPD proceeded as well as the comparable CPD reaction in Task II. MCPD seemed to be more thermally stable in our oligomerizations than DCPD. In all four of our variable concentration oligomerizations, the CPD dimer concentration in the final product was less than the MCPD dimer concentration.

Different reagent ratios gave different product consistencies but since contractual constraints did not permit isolation of individual isomers, one cannot speculate as to their phase contribution. Increased MCPD dimer in HKM 3/19/79(1) product may be the reason that it is a liquid at room temperature.

Isolating the CPD-MCPD trimers by vacuum distillation progressed as well as isolating the CPD trimers in Task II.

However, in attempting to fractionate the higher-boiling tetramers at 162°C and .05 mm HG pressure, decomposition in the distillation pot produced lower-boiling monomers and dimers (Figure 33). This precarious phenomenon might be looked upon as a fortunate turn of events when one considers that some of the higher molecular weight cooligomers may be purposely decomposed and recycled, after isolating trimers, to form more trimers in subsequent cooligomerizations.

To test this theory, 75.3 g of HKM 3/9/79(1) distillation, Cut #7, which was decomposition product from the above-mentioned distillation, was stirred and heated to 174°C for 54 hours in a glass Fischer-Porter pressure bottle and the recovered 70.3 g of wax-like product displayed an analytical simulated distillation scan (Figure 35) quite similar to that produced from initial cooligomerizations using commercial feed stocks (Figures 27-30).

SECTION IV

CONCLUSIONS

A. Preparation of Diamantane - Task I

Binor-S may be quantitatively isomerized to diamantane by hydrogenolyzing the cyclopropane rings of Binor-S, with a 5% rhodium catalyst, to tetrahydro Binor-S, and then isomerizing the tetrahydro Binor-S with aluminum chloride to diamantane.

We have successfully employed a process where 1 wt.% of a 5% rhodium on alumina (or carbon) is stirred at 1200 rpm at a maximum of 250°C and 430 psig hydrogen pressure with neat Binor-S for 8 hours to produce tetrahydro Binor-S.

Then, one part by weight of $AlCl_3$ is charged to 3-6 parts of THB-S dissolved in 10-20 parts of dichloromethane. This mixture is stirred, warmed to reflux, and held there for 6 hours. A "raw" diamantane crystalline solid phase develops which may be filtered from the supernatant and recrystallized from 4 parts by weight of toluene to produce 97% pure diamantane.

B. Preparation of exo-tetrahydrotri (cyclopentadiene) - Task II

Isomerized cyclopentane trimer has been conveniently prepared from cyclopentadiene dimer by oligomerizing CPD, isolating the trimer by vacuum distillation, hydrogenating this oligomer, isomerizing it with a Friedal-Crafts catalyst, and purifying the resultant "raw" exo-THTriCPD by percolating it through adsorbant clays or by vacuum distillation.

Oligomerization is accomplished by stirring DCPD at 170°-200°C for 7-10 hours. The trimer may be extracted from the oligomeric mixture at a 325° - 340°C head temperature under .4 mm Hg pressure. This diolefinic trimer may then be saturated by stirring it with 6 - 8% Nickel on Kieselguhr catalyst at 128° - 147°C under 197 psig hydrogen pressure for 2.2 - 3.4 hours. To isomerize the resultant tricyclopentane, it is dissolved in an equal weight of dichloromethane, saturated with hydrogen chloride gas and stirred with 9 - 15 wt.% $AlCl_3$ at 0° - 20°C for 3-9 hours. (Observations indicate that HCl saturation increases isomerization rates but that solid $AlCl_3$ should be present and washed free of developing sludges with a solvent such as dichloromethane for rapid isomerization continuation.) Dichloromethane is stripped from the resultant oil, creating two liquid phases. The trimer supernatant is decanted through diatomaceous earth and then scrubbed with an equal part of saturated KCl-HOH

solution. "Raw" exo-tetrahydrotri(cyclopentadiene) may be purified by passing it through 1/6 its weight of serpentine clay at room temperature, or by distilling at an 81°-108°C head temperature under .04-.09 mm Hg pressure.

C. Preparation of Hydrogenated Product of Isomerized endo, endo-Di(Norbornadiene) - Task III

For this process clean norbornadiene NN≡ dimer and 5-15 wt.% of dry acid alumina (Harshaw Al-1602 powder or tablets) are mixed together in a suitable reactor at 24°C and then deaerated with an inert gas such as nitrogen while stirring. After deaeration the mixture is heated gradually under an inert atmosphere to a temperature of 170°C, at which time the isomerization rate becomes noticeable. During this period some moisture may be driven off some catalysts and means should be provided for its exclusion from the reactor.

The reaction temperature should be increased until the desired isomerization rate is reached or to a mazimum of 230°C. When the planned conversion is obtained, 5-16 hours, the reactor may be cooled and the contents filtered.

This isomerized olefinic mixture may be completely and rapidly hydrogenated in much the same way as the fuel RJ-5. It is heated in a suitable stirred reactor using 10 wt.% of nickel on Kieselguhr catalyst (Harshaw Ni-0104P) at 115 psig of hydrogen and a temperature of 115°C.

When saturation is complete the reactor may be cooled and the contents filtered - producing a final product. Should specifications require a minimum viscosity, this final product may be distilled to eliminate trace NBD tetramer.

To date, this approach is our most promising lead for converting NBD endo, endo hexacyclic dimer into an operational fuel.

D. Isomerization of C_{18} Tetrahydrotri(methylcyclopentadiene) - Task IV A

Progress toward completing Task IV continued through: cooligomerization of cyclopentadiene with methylcyclopentadiene; isolation of the trimer cooligomer; to an investigation which recycled decomposition fractions of cracked cooligomer by-products to form additional trimer cooligomers.

Various cooligomerization reactions were made, combining different molar concentrations of MCPD dimer to CPD dimer. Our procedure consisted of mixing molar ratios of 0.5-2.0 of MCPD dimer to CPD dimer in a one gallon Hastelloy "B", stirred autoclave and heating under an inert atmosphere and autogenous pressure to between 190° and 207°C

intermittantly for 30-41 hours. These produced cooligomeric mixtures containing from 41.2-43.6% CPD-MCPD trimers with less than 3% polymers vaporizing higher than 350°C.

A trimer fraction was isolated via vacuum distillation by taking the cut boiling from 35°-110°C at 0.04-0.13 mm Hg pressure. Unless it is desirable to decompose higher molecular weight cooligomers, care must be exercised to maintain the distillation pot diolefinic-liquid temperature below 162°C at 0.05 mm Hg pressure since under these conditions the cooligomers remaining in the pot begin cracking into smaller components. However, these smaller components are CPD and MCPD monomers and dimers which may be used in subsequent cooligomerizations to make more trimers.

SECTION V

RECOMMENDATIONS

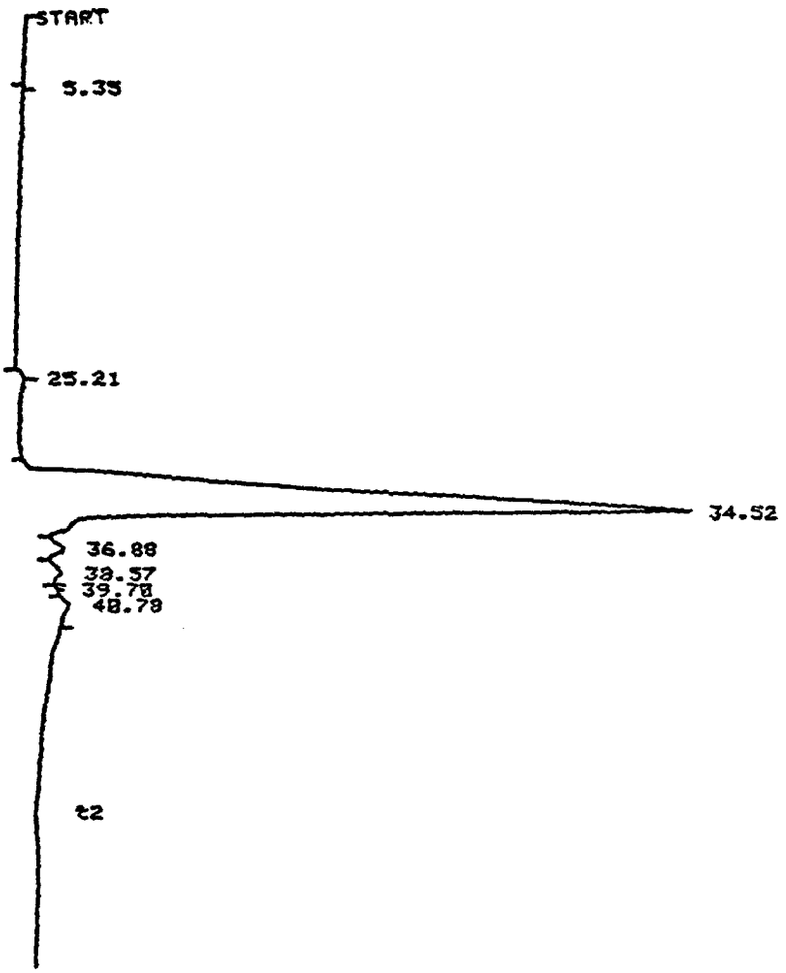
To further the cause of this project we suggest that more energies be devoted to the preparation of hydrogenated products of isomerized endo, endo-Di (norbornadiene) - Task III.

A small number of commercially available acidic aluminas have been found to be active for this isomerization reaction, whereas several have proven to be ineffective. It would be wise to determine what bestows activity to an alumina and how to control this activity. Along this line, calcination temperature and residual water content appear to be critical. Residual contents of non-protonic cations on the surface of the alumina may be extremely detrimental to activity and this should be fully examined. Small amounts of silica in the alumina may be beneficial. Type of alumina, surface areas and particle size also warrant investigation, particularly with the intent of operating this isomerization in a continuous, fixed-bed mode. Acidic molecular sieves, such as 13-X, should be evaluated and compared with acidic aluminas. The effect of temperature during isomerization in controlling isomer distribution should be determined to enable the production of compounds of minimum freeze point. Exact relations between extent of conversion of starting material and concentration of tetramer in the product should be determined at a number of isomerization temperatures. Physical properties should be correlated with isomer distribution in the hydrogenated products, major and minor isomers should be separated and purified by crystallization at low temperatures from ether, and the ideal solution equilibrium freezing points versus mole fraction curves should be determined for these compounds.

To improve our high energy fuels and understanding of their production we recommend that more time be devoted to the isomerization of C_{18} tetrahydrotri (methylcyclopentadiene) - Task IV.

During the preparation of THTri-MeCPD optimum conditions should be defined for obtaining maximum yields of trimer. Complete sets of property data should be obtained for the unisomerized, hydrogenated trimer since it is already a complexed liquid mixture of largely endo-isomers with high viscosity and pour point (13). These data should be compared with those of the isomerized products.

Binor-S Cut #13 charged to 6-23-78 -.4 µℓ



HP 5830A
AREA %

RT	AREA	AREA %
5.35	337	0.022
25.21	2743	0.179
34.52	1487000	96.931
36.88	22140	1.444
38.57	10370	0.676
39.70	107	0.007
40.78	10600	0.691

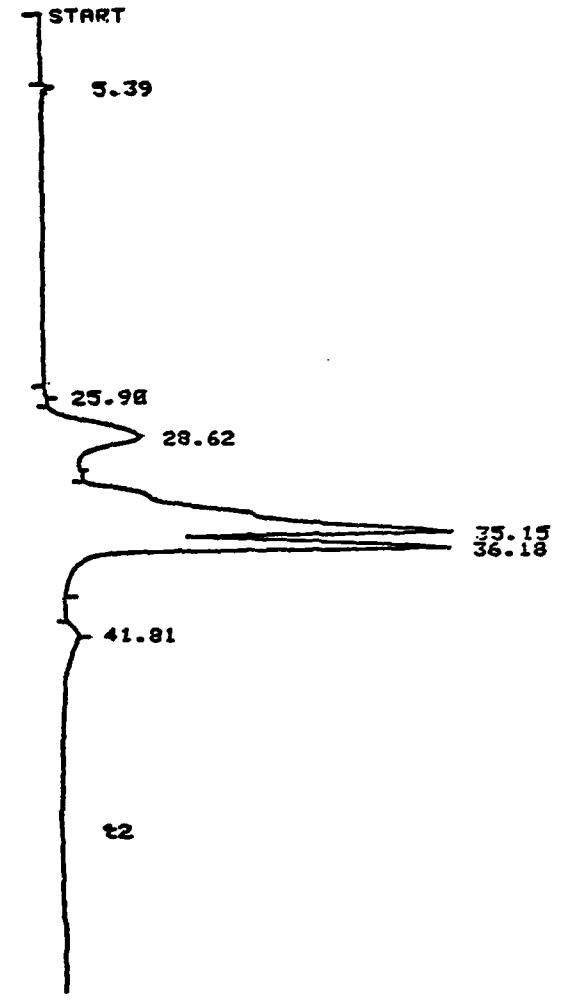
XF: 1.0000 E+ 0

TEMP1	141	143
TIME1	27.0	
RATE	10.00	
TEMP2	224	
TIME2	30.0	
INJ TEMP	275	275
TCD TEMP	270	270
AUX TEMP	150	150
OVEN MAX	230	

CHT SPD	0.30
ATTN 2↑	7
TCD SGNL	A
SLP SENS	0.07
AREA REJ	1
FLOW	21
FLOW	14
OPTN	3098
55.0 TEMP2	230

Figure 1

HKM 6-23-78(1) Sample #1 -.4 µℓ



hp 5830A
AREA %

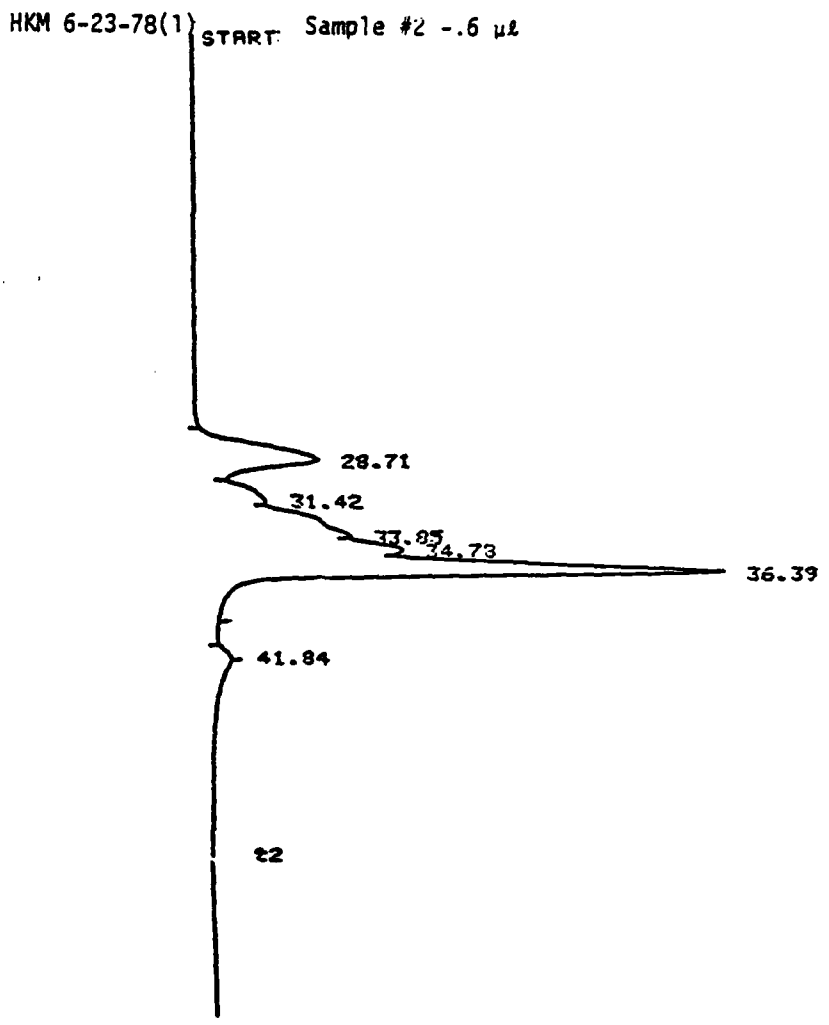
RT	AREA	AREA %
5.39	2903	0.238
25.90	[illegible]	[illegible]
28.62	146500	12.017
35.15	[illegible]	[illegible]
36.18	348200	[illegible]
41.81	2535	0.208

XF: 1.0000 E+ 0

TEMP1	141	141
TIME1	27.0	
RATE	10.00	
TEMP2	224	
TIME2	30.0	
INJ TEMP	275	275
TCD TEMP	270	270
AUX TEMP	150	150
OVEN MAX	230	

CHT SPD	0.30
ATTN 2↑	7
TCD SGNL	A
SLP SENS	0.07
AREA REJ	1
FLOW A	21
FLOW B	19
OPTN	3098
55.0 TEMP2	230

Figure 2



hp 5830A
AREA %

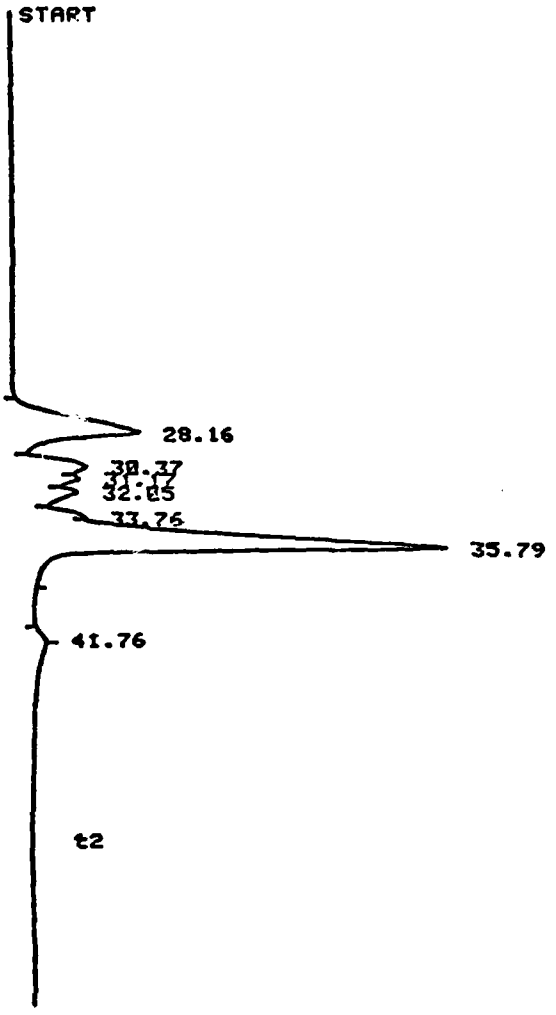
RT	AREA	AREA %
28.71	241500	15.215
31.42	77240	4.866
33.85	315100	19.852
34.78	263100	16.576
36.39	688000	43.345
41.84	2331	0.147

XF: 1.0000 E+ 0

TEMP1	141	141
TIME1	27.0	
RATE	10.00	
TEMP2	224	
TIME2	30.00	
INJ TEMP	275	275
TCD TEMP	270	270
AUX TEMP	150	150
OVEN MAX	230	
CHT SPD	0.38	
ATTN 2↑	7	
TCD SGNL	A	
SLP SENS	0.87	
AREA REJ	1	
FLOW A	21	
FLOW B	19	
OPTN	3039	
35.0	TEMP2	230

Figure 3

HKM 6-23-78(1) Sample #3 -.5 µℓ



HP 5830A
AREA %

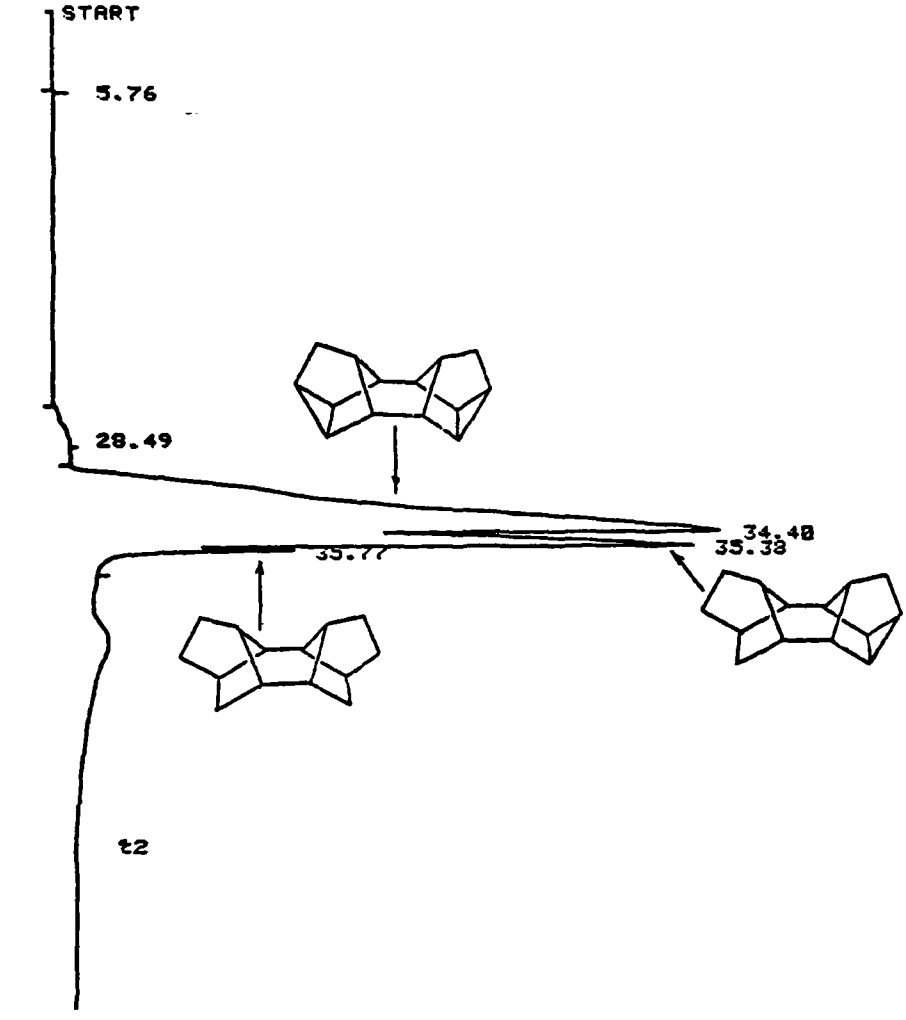
RT	AREA	AREA %
28.16	213408	19.759
30.37	74900	6.935
31.17	46710	4.325
32.05	59040	5.467
33.76	40980	3.794
35.79	643800	59.537
41.76	1976	0.183

XF: 1.0000 E+ 0

TEMP1	141	141
TIME1	27.0	
RATE	10.00	
TEMP2	224	
TIME2	30.0	
INJ TEMP	275	275
TCD TEMP	270	270
AUX TEMP	150	150
OVEN MAX	230	
CHT SPD	0.30	
ATTN 2↑	7	
TCD SGNL	A	
SLP SENS	0.07	
AREA REJ	1	
FLOW A	21	
FLOW B	19	

Figure 4

VPC scan of sample from Binor-S hydrogenolysis--HKM 7-26 (1) 150 Min.



HP 5830A
AREA %

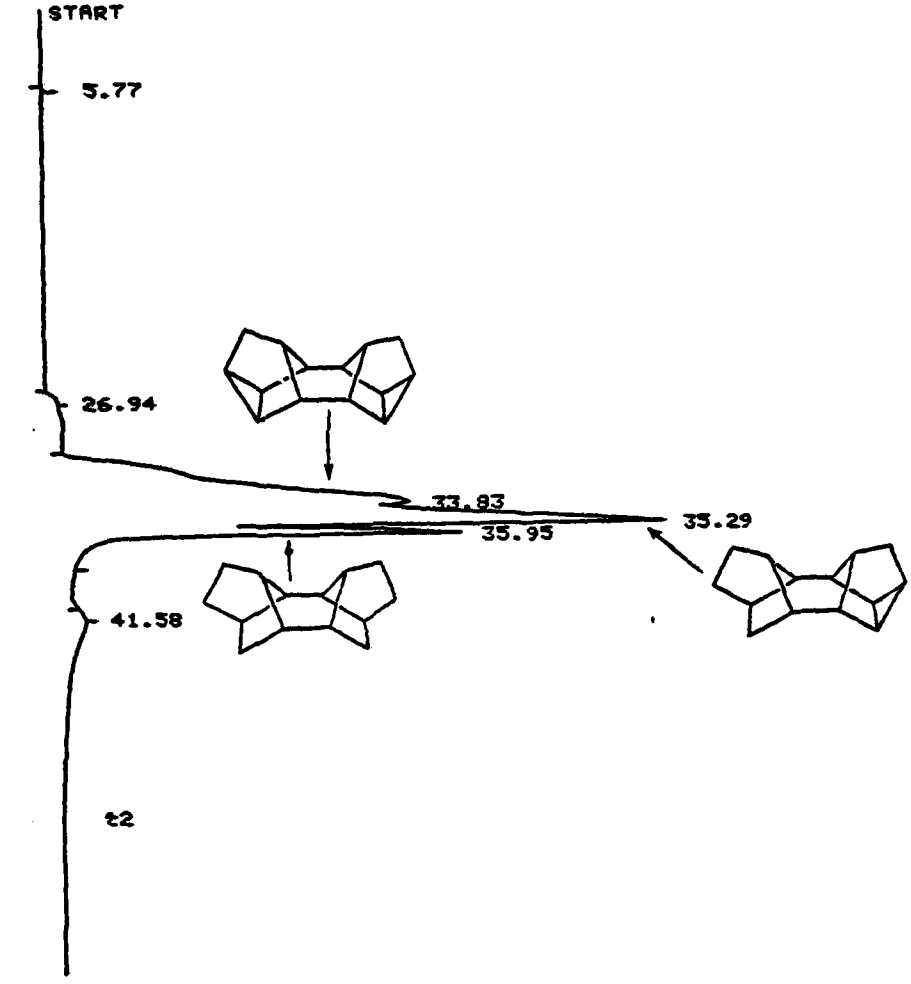
RT	AREA	AREA %
5.76	185	0.008
28.49	2271	0.101
34.40	1592000	71.056
35.38	554400	24.745
35.77	91640	4.090

XF: 1.0000 E+ 0

TEMP1	141	142
TIME1	27.0	
RATE	10.00	
TEMP2	224	
TIME2	30.0	
INJ TEMP	275	275
TCD TEMP	270	270
AUX TEMP	150	150
OVEN MAX	230	
CHT SPD	0.30	
ATTN 2↑	7	
TCD SGNL	A	
SLP SENS	0.07	
AREA REJ	1	
FLOW A	20	
FLOW B	20	
OPTN	3090	
55.0 TEMP2	230	

Figure 5

VPC scan of sample from Binor-S hydrogenolysis—HKM 7-26(1) 170 min.



hp 5830A
AREA %

RT	AREA	AREA %
5.77	341	0.018
26.94	1412	0.074
33.83	823400	42.934
35.29	803000	41.870
35.95	289200	15.080
41.58	487	0.025

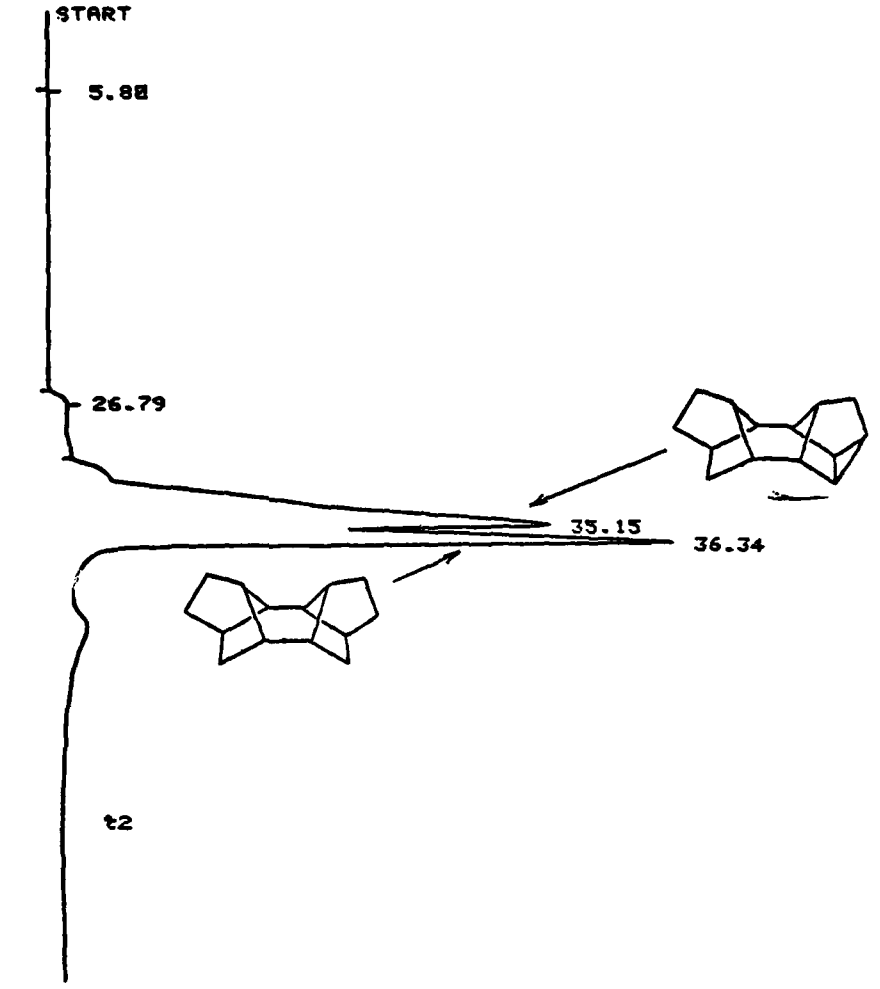
XF: 1.0000 E+ 0

TEMP1	141	141
TIME1	27.0	
RATE	10.00	
TEMP2	224	
TIME2	30.0	
INJ TEMP	275	275
TCD TEMP	270	270
AUX TEMP	150	150
OVEN MAX	230	

CHT SPD	0.30
ATTN 2↑	7
TCD SGNL	A
SLP SENS	0.07
AREA REJ	1
FLOW A	20
FLOW B	20
OPTN	3098
55.0 TEMP2	230

Figure 6

VPC scan of sample from Binor-S hydrogenolysis--HKM 7-26(1) 190 min.



HP 5830A
AREA %

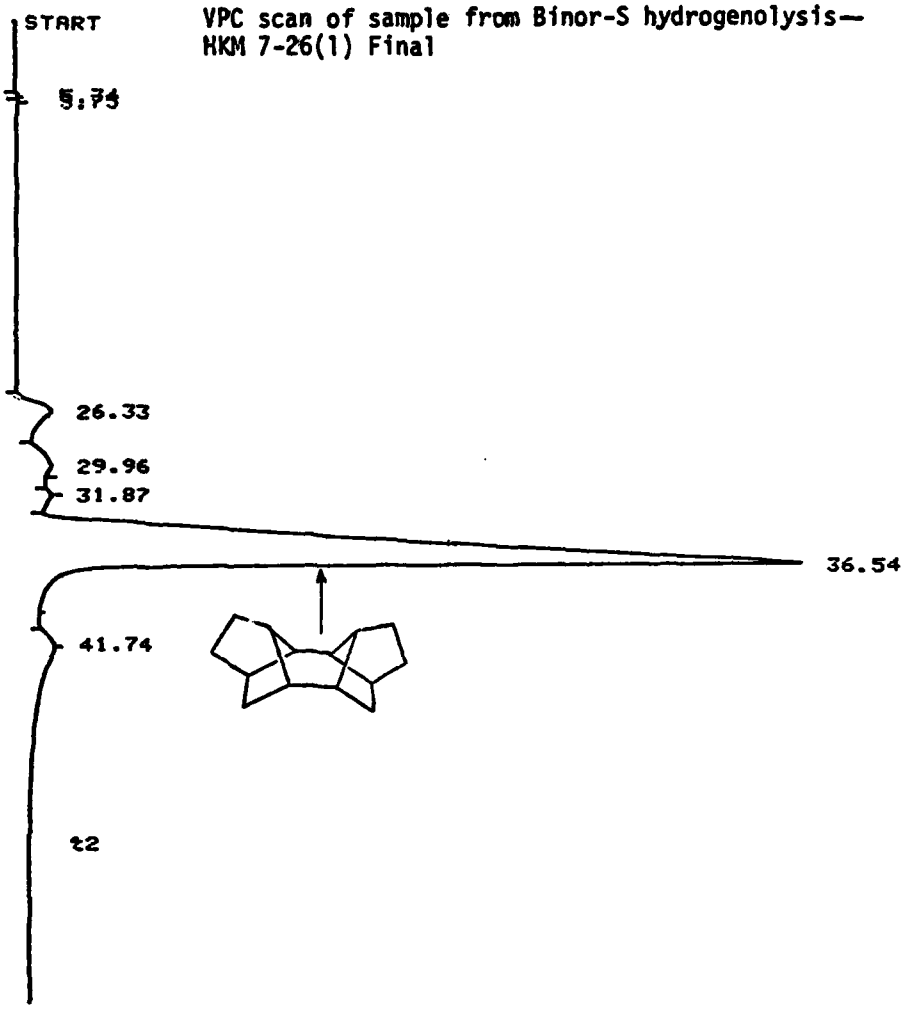
RT	AREA	AREA %
5.80	181	0.005
26.79	7717	0.201
35.15	1146[illegible]00	62.093
36.34	695800	37.700

XF: 1.0000 E+ 0

TEMP1	141	142
TIME1	27.0	
RATE	10.00	
TEMP2	224	
TIME2	30.0	
INJ TEMP	275	275
TCD TEMP	270	270
AUX TEMP	150	150
OVEN MAX	230	
CHT SPD	0.30	
ATTN 2↑.	7	
TCD SGNL	A	
SLP SENS	0.07	
AREA REJ	1	
FLOW A	21	
FLOW B	20	
OPTN	3098	
55.0 TEMP2	230	

Figure 7

VPC scan of sample from Binor-S hydrogenolysis—
HKM 7-26(1) Final



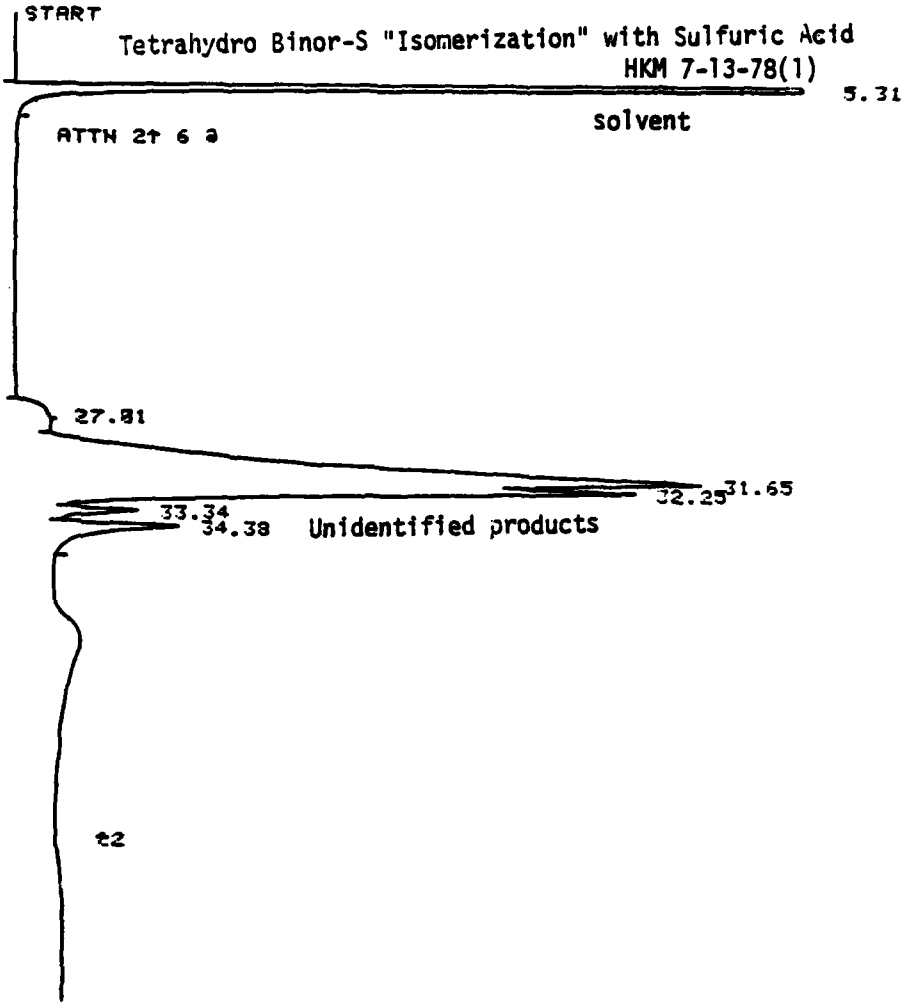
HP 5830A
AREA %

RT	AREA	AREA %
5.34	505	0.029
5.75	179	0.010
26.33	51970	3.006
29.96	18850	1.090
31.87	473	0.027
36.54	1656000	95.779
41.74	1002	0.058

XF: 1.0000 E+ 0

TEMP1	141	143
TIME1	27.0	
RATE	10.00	
TEMP2	224	
TIME2	30.0	
INJ TEMP	275	275
TCD TEMP	270	270
AUX TEMP	150	150
OVEN MAX	230	
CHT SPD	0.30	
ATTN 2↑	7	
TCD SGNL	A	
SLP SENS	0.07	
AREA REJ	1	
FLOW A	20	
FLOW B	20	
OPTN	3098	
55.0 TEMP2	230	

Figure 8



hp 5830A
AREA %

RT	AREA	AREA %
5.31	3126000	77.626
27.81	4296	0.107
31.65	626400	15.555
32.25	199700	4.959
33.34	21290	0.529
34.38	49340	1.225

XF: 1.0000 E+ 0

TEMP1	141	141
TIME1	27.0	
RATE	10.00	
TEMP2	224	
TIME2	30.0	
INJ TEMP	275	275
TCD TEMP	270	270
AUX TEMP	150	150
OVEN MAX	230	
CHT SPD	0.30	
ATTN 2↑	6	
TCD SGNL	A	
SLP SENS	0.07	
AREA REJ	1	
FLOW A	21	
FLOW B	20	
OPTN	3090	
99.0 TEMP2	230	

gure 9

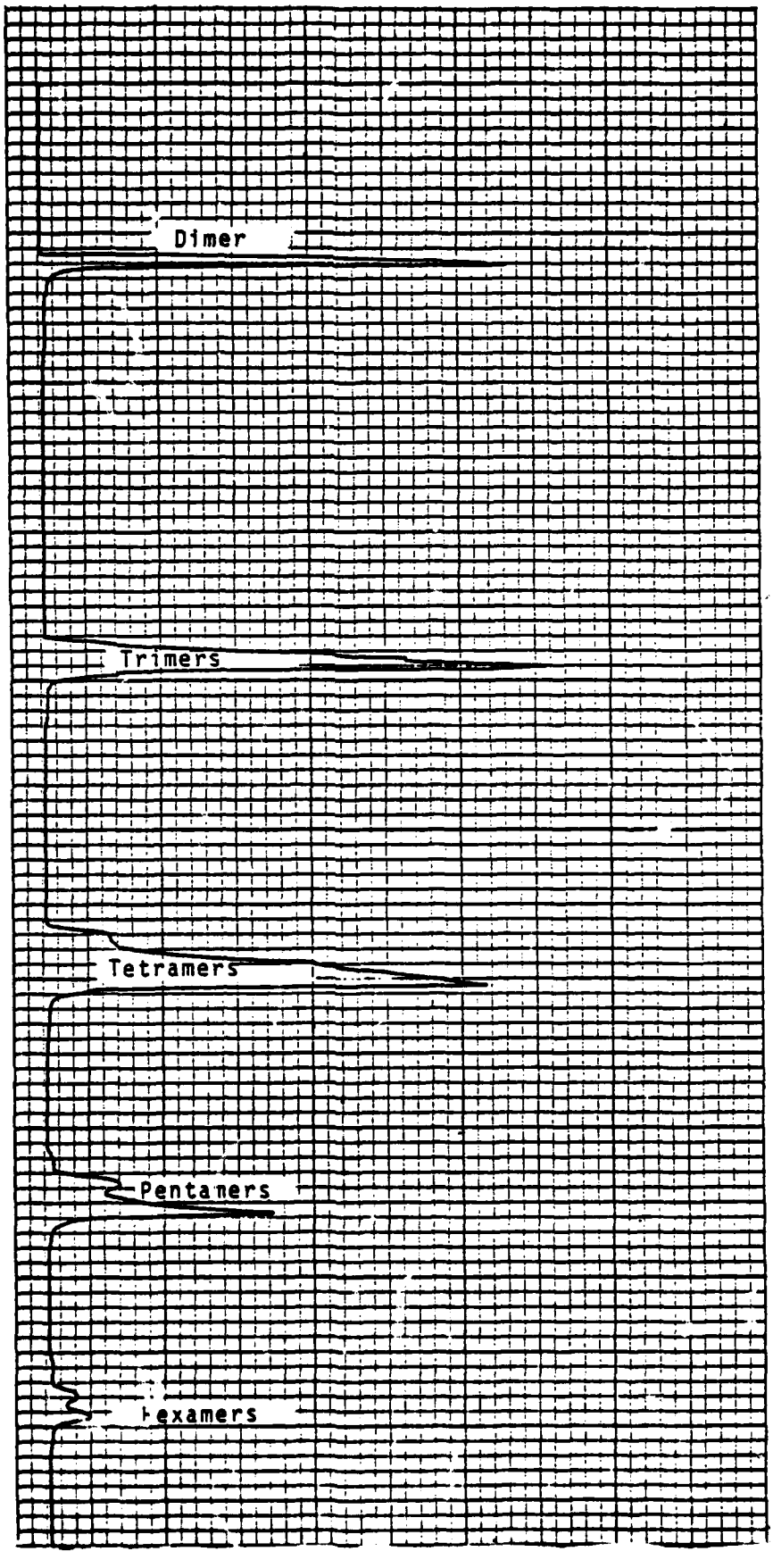
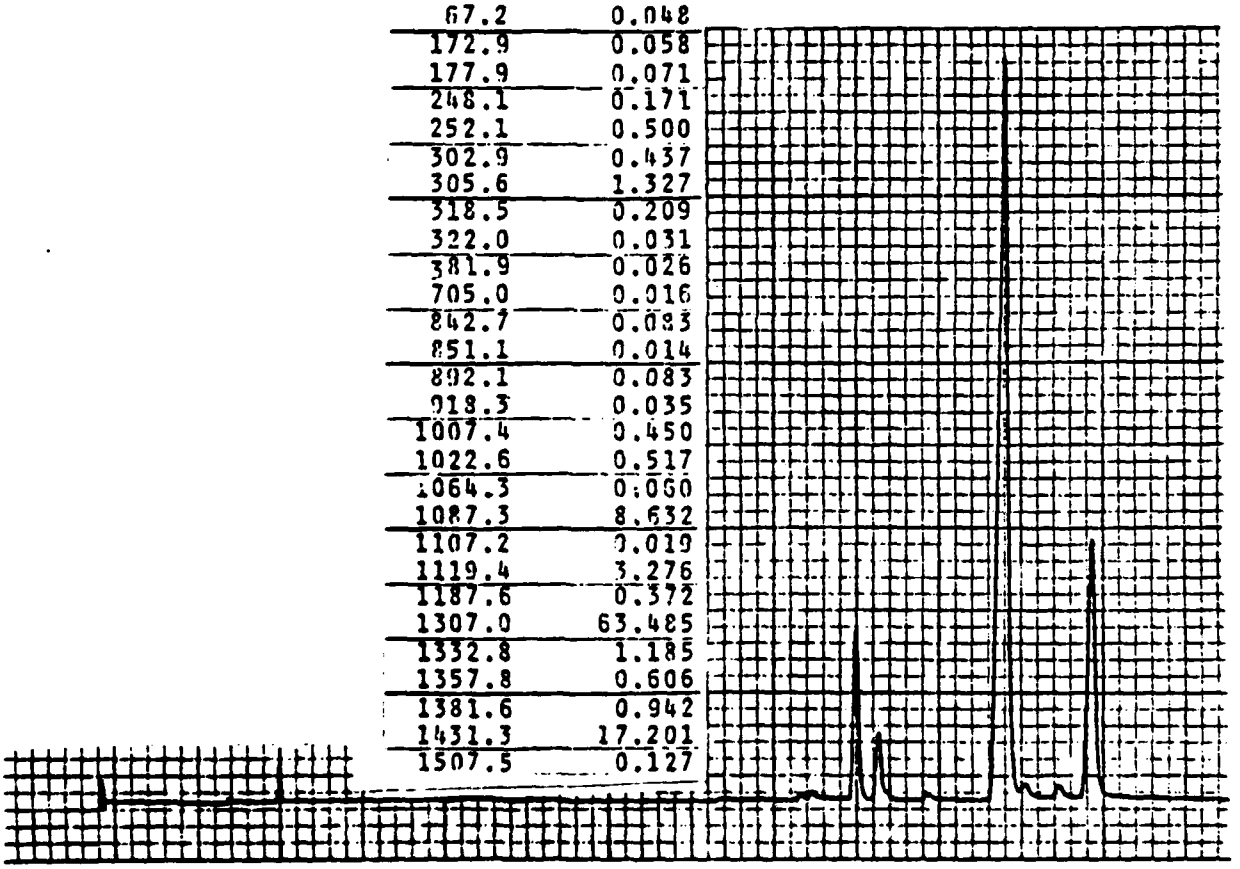


Figure 10

HKM 10-17-78(1) Cut #2 Cyclopentadiene Trimer Charge

63.2	0.019
67.2	0.048
172.9	0.058
177.9	0.071
248.1	0.171
252.1	0.500
302.9	0.437
305.6	1.327
318.5	0.209
322.0	0.031
381.9	0.026
705.0	0.016
842.7	0.083
851.1	0.014
892.1	0.083
918.3	0.035
1007.4	0.450
1022.6	0.517
1064.3	0.060
1087.3	8.632
1107.2	0.019
1119.4	3.276
1187.6	0.372
1307.0	63.485
1332.8	1.185
1357.8	0.606
1381.6	0.942
1431.3	17.201
1507.5	0.127

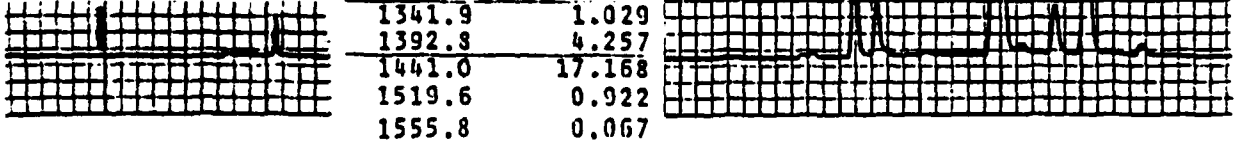


150'OS 138 Chromatographic column

Figure 1i

HKM 10-17-78(1) 60 minute sample Cyclopentadiene Trimers

115.3	0.034
138.4	0.151
146.3	0.752
151.6	0.090
155.0	0.194
158.0	0.551
176.1	0.108
204.9	0.025
225.8	0.028
246.9	0.449
251.3	0.725
262.5	0.016
287.6	0.028
461.8	0.045
465.0	0.037
669.5	0.078
675.1	0.031
683.9	0.080
776.2	0.047
958.1	0.046
1012.1	0.387
1029.3	0.432
1093.3	8.815
1126.5	3.942
1195.6	1.332
1207.7	0.071
1211.2	1.735
1312.4	54.363
1341.9	1.029
1392.8	4.257
1441.0	17.168
1519.6	0.922
1555.8	0.067
1691.4	0.017
1762.3	0.879
1776.7	0.568

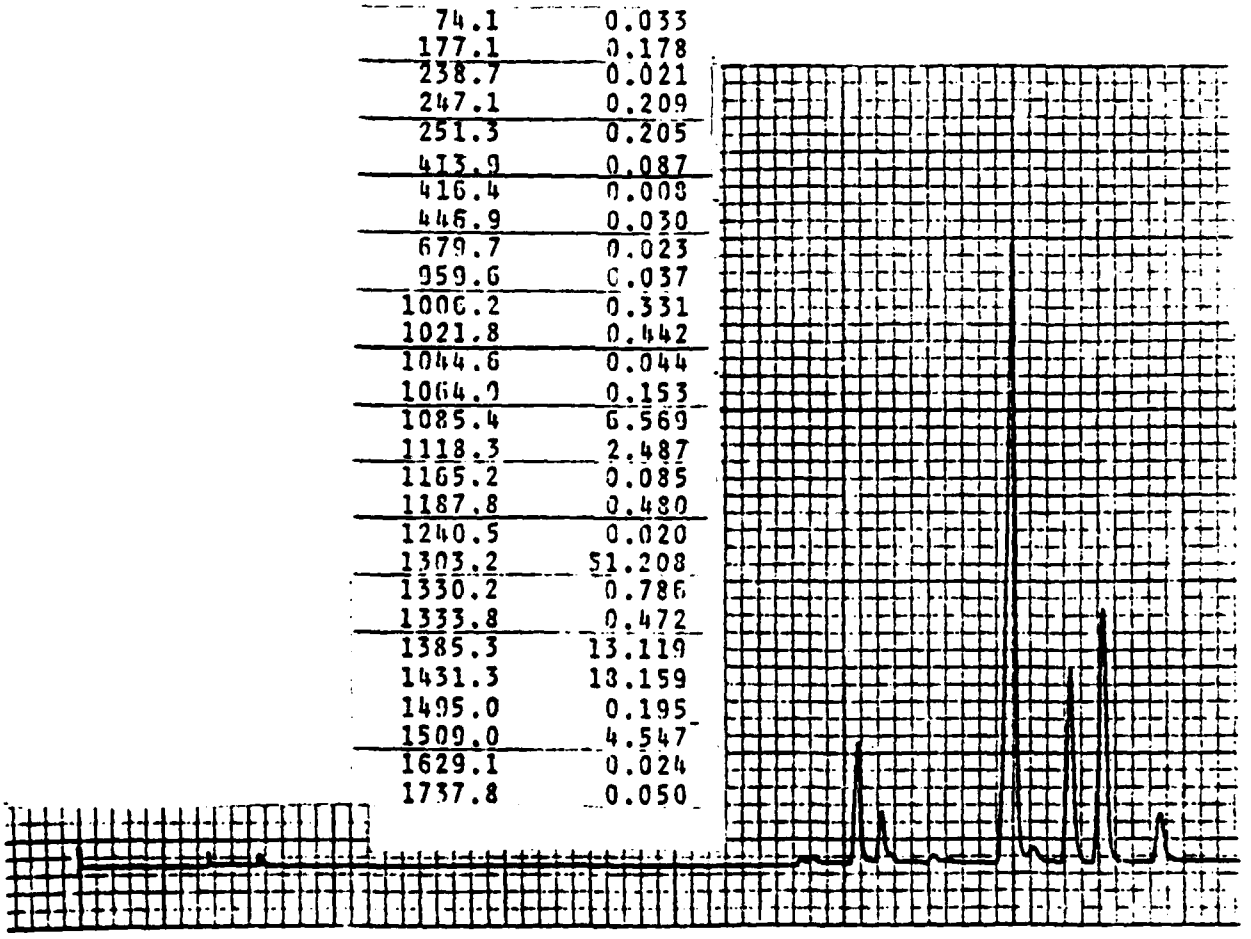


150'OS 138 Chromatographic column

Figure 12

HKM 10-17-78 (1) 492 Minute Sample Cyclopentadiene Trimers

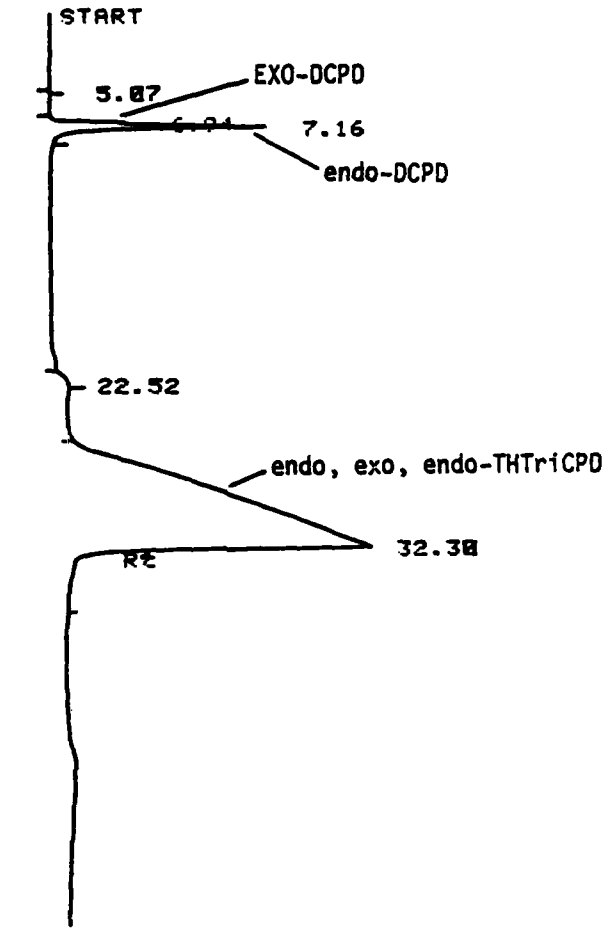
74.1	0.033
177.1	0.178
238.7	0.021
247.1	0.209
251.3	0.205
413.9	0.087
416.4	0.008
446.9	0.030
679.7	0.023
959.6	0.037
1006.2	0.331
1021.8	0.442
1044.6	0.044
1064.9	0.153
1085.4	6.569
1118.3	2.487
1165.2	0.085
1187.8	0.480
1240.5	0.020
1303.2	51.208
1330.2	0.786
1333.8	0.472
1385.3	13.119
1431.3	13.159
1495.0	0.195
1509.0	4.547
1629.1	0.024
1737.8	0.050



150'OS 138 Chromatographic Column

Figure 13

HKM 11-29 78(1) Charged TH TriCPD from 10-27 (1)



hp 5830A

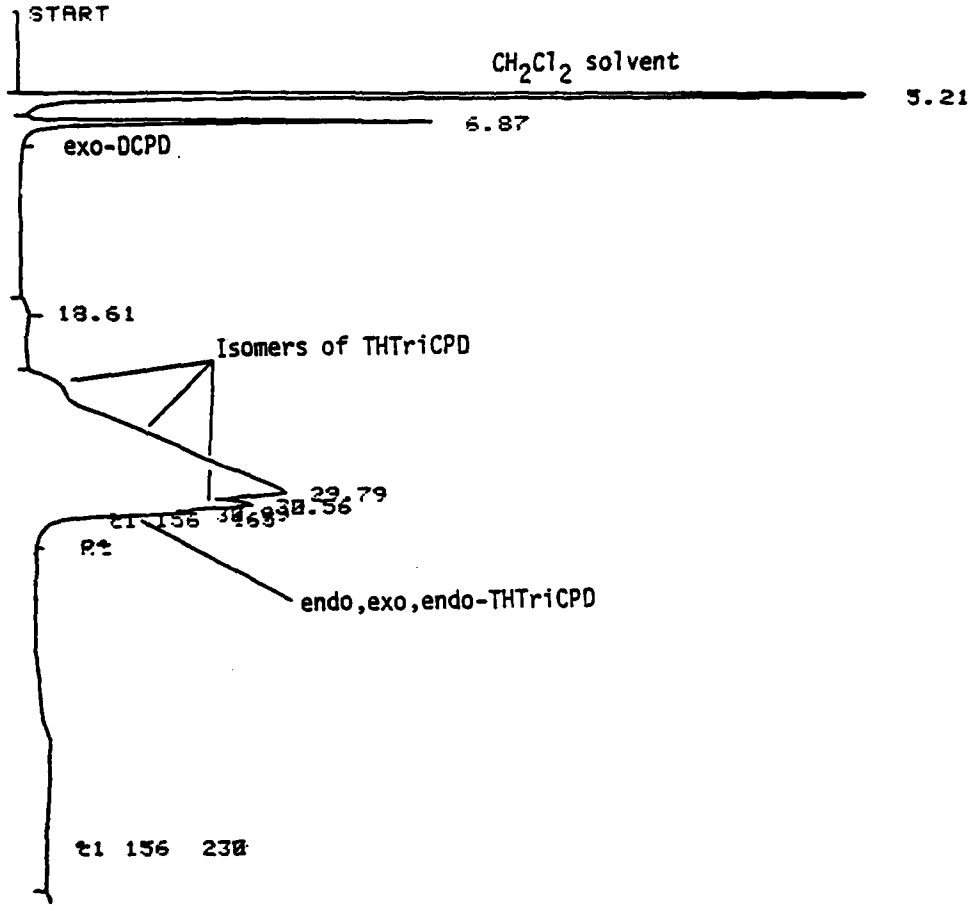
NO	METHOD	RT	AREA	AREA %
		5.07	123	0.010
		6.94	13780	1.078
		7.16	69700	5.453
		22.52	2689	0.210
		32.30	1192000	93.249

XF: 1.0000 E+ 0

TEMP1	156	172
TIME1	22.0	
RATE	1.00	
TEMP2	230	
TIME2	20.0	
INJ TEMP	275	275
TCD TEMP	270	270
AUX TEMP	150	150
OVEN MAX	230	
CHT SPD	0.30	
ATTN 2↑	7	
TCD SGNL	A	
SLP SENS	0.07	
AREA REJ	1	
FLOW A	21	
FLOW B	21	
OPTN	3098	
33.0 RATE	30.00	

Figure 14

HKM 11 29-78(1) THTriCPD 95 minutes after $AlCl_3$



hp 5830A

NO	METHOD RT	AREA	AREA %
	5.21	761600	33.579
	6.87	124000	5.467
	18.61	2166	0.095
	29.79	1142000	50.351
	30.56	160600	7.081
	30.99	77720	3.427

XF: 1.0000 E+ 0

TEMP1	156	156
TIME1	22.0	
RATE	1.00	
TEMP2	230	
TIME2	20.0	
INJ TEMP	275	275
TCD TEMP	270	270
AUX TEMP	150	150
OVEN MAX	230	
CHT SPD	0.30	
ATTN 2↑	7	
TCD SGNL	A	
SLP SENS	0.07	
AREA REJ	1	
FLOW A	21	
FLOW B	20	
OPTN	3090	
33.0	RATE	30.00

Figure 15

HKM-11-29-78 (1) Final; 160 minutes after $AlCl_3$

High Resolution Capillary GC using a 150' OS138 column

ELUTION TIME (SEC)	AREA PCT
38.2	0.011
160.8	0.020
178.3	0.054
203.9	0.019
208.4	0.015
214.1	0.013
220.0	0.134
234.4	0.066
245.6	0.039
255.5	5.698
274.4	0.066
308.1	0.004
312.1	0.024
321.0	0.018
377.2	0.015
546.8	0.006
578.2	0.022
601.4	0.017
709.7	0.007
718.4	0.038
791.6	0.005
798.0	0.002
807.2	0.043
814.3	0.012
859.6	0.087
871.5	0.385
899.2	0.024
921.1	0.569
995.0	0.015
1005.5	0.071
1032.3	0.004
1053.6	0.188
1081.7	0.244
1090.1	0.170
1103.9	0.155
1134.2	0.568
1240.2	13.928
1277.2	0.279
1301.0	0.005
1344.9	0.010
1362.5	0.344
1432.8	50.704
1459.0	0.014
1508.2	0.016
1577.2	20.610
1636.8	4.323
1650.2	0.830
1673.4	0.038
1819.3	0.015
1836.5	0.003
2032.6	0.012
2106.9	0.011
2147.6	0.014
2279.0	0.010
2338.3	0.005

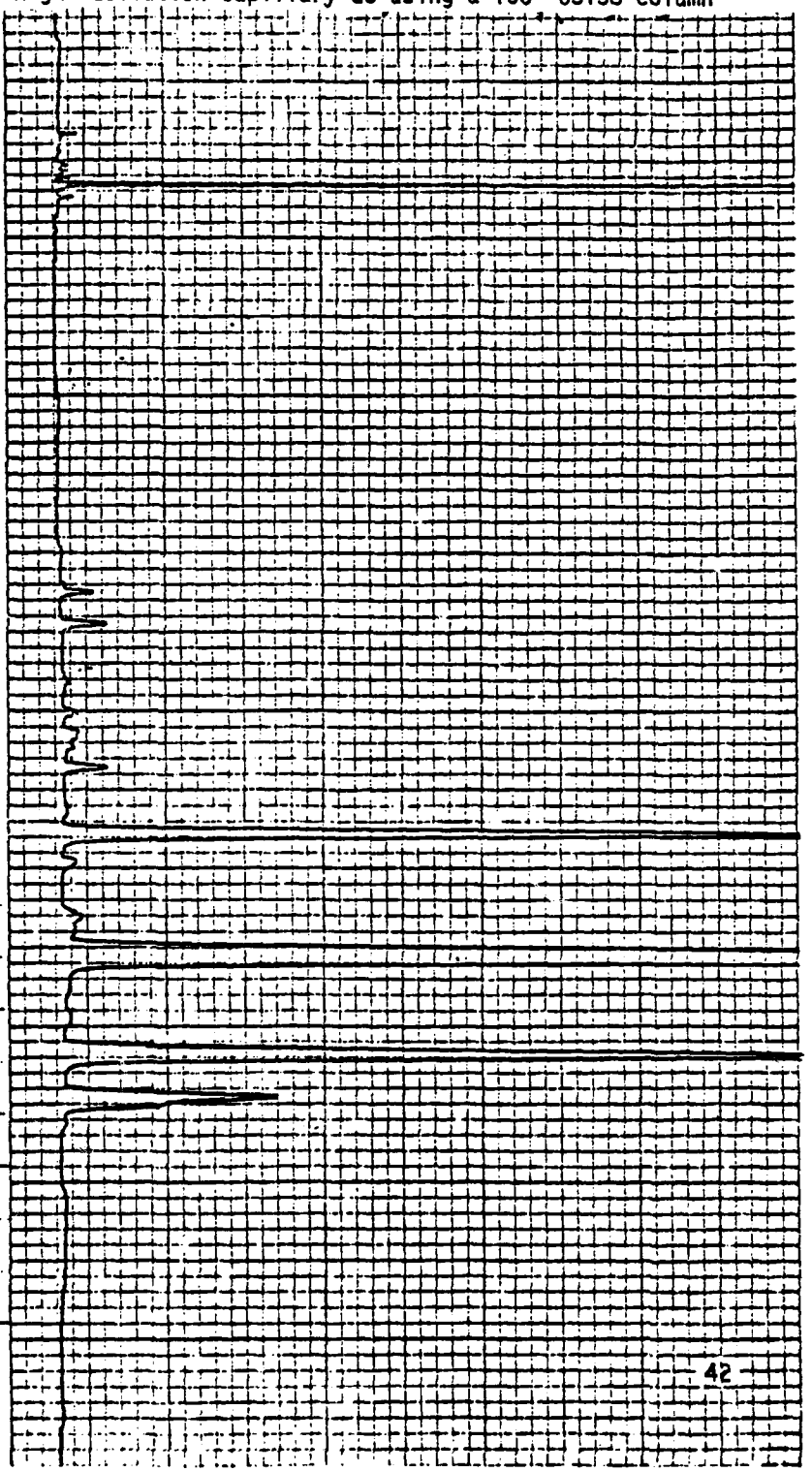
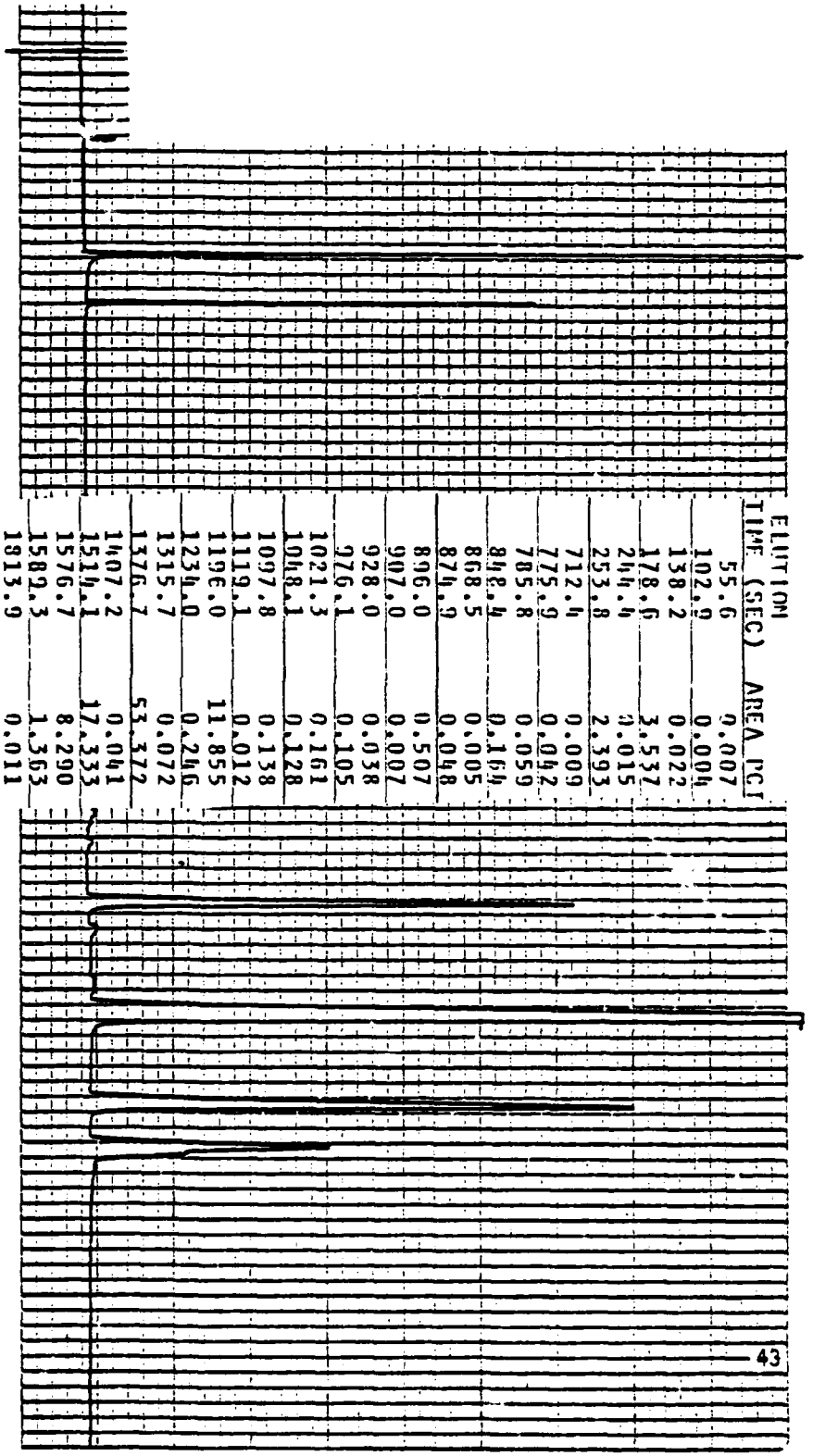


Figure 16

HKM 12-11-78 (1) Isomerized THTriCPD High Resolution Capillary G.C. using a 150' OS 138 column.



ELUTION TIME (SEC)	AREA PCT
55.6	0.007
102.9	0.004
138.2	0.022
178.6	3.537
244.4	3.015
253.8	2.393
712.4	0.009
775.9	0.042
785.8	0.059
848.4	0.164
868.5	0.005
874.9	0.048
896.0	0.507
907.0	0.007
928.0	0.038
976.1	0.105
1021.3	0.161
1048.1	0.128
1097.8	0.138
1119.1	0.012
1196.0	11.855
1234.0	0.246
1315.7	0.072
1376.7	53.372
1407.2	0.041
1514.1	17.333
1576.7	8.290
1589.3	1.363
1813.9	0.011
1959.1	0.011
2053.2	0.006

Figure 17

HKM 1-4-79 (1) Isomerized THTriCPD High Resolution
Capillary G.C. using a 150' OS 138 column

TIME (SEC)	AREA PCT
43.1	0.023
72.4	0.010
181.1	1.705
207.4	0.010
245.8	0.016
249.8	0.034
259.5	2.445
279.6	0.029
308.2	0.020
309.9	0.000
396.3	0.009
420.6	0.010
503.7	0.044
528.0	0.016
531.2	0.015
587.0	0.018
625.3	0.020
644.1	0.008
656.0	0.011
710.7	0.017
749.1	0.008
843.1	0.014
869.4	0.057
880.4	0.404
930.2	0.491
975.9	0.008
1013.9	0.050
1062.3	0.192
1089.6	0.074
1111.2	0.079
1142.4	0.531
1201.5	0.016
1210.1	0.051
1245.9	12.829
1284.6	0.190
1323.8	0.039
1337.4	0.984
1361.0	0.012
1393.5	0.045
1435.0	54.696
1497.7	0.008
1578.2	19.164
1640.0	4.557
1654.3	0.681
1673.7	0.062
1684.2	0.058
1744.0	0.013
1788.8	0.080
1865.0	0.026
1914.1	0.005
1975.0	0.012
2006.5	0.009
2040.4	0.007
2083.9	0.005
2107.2	0.017
2130.5	0.020

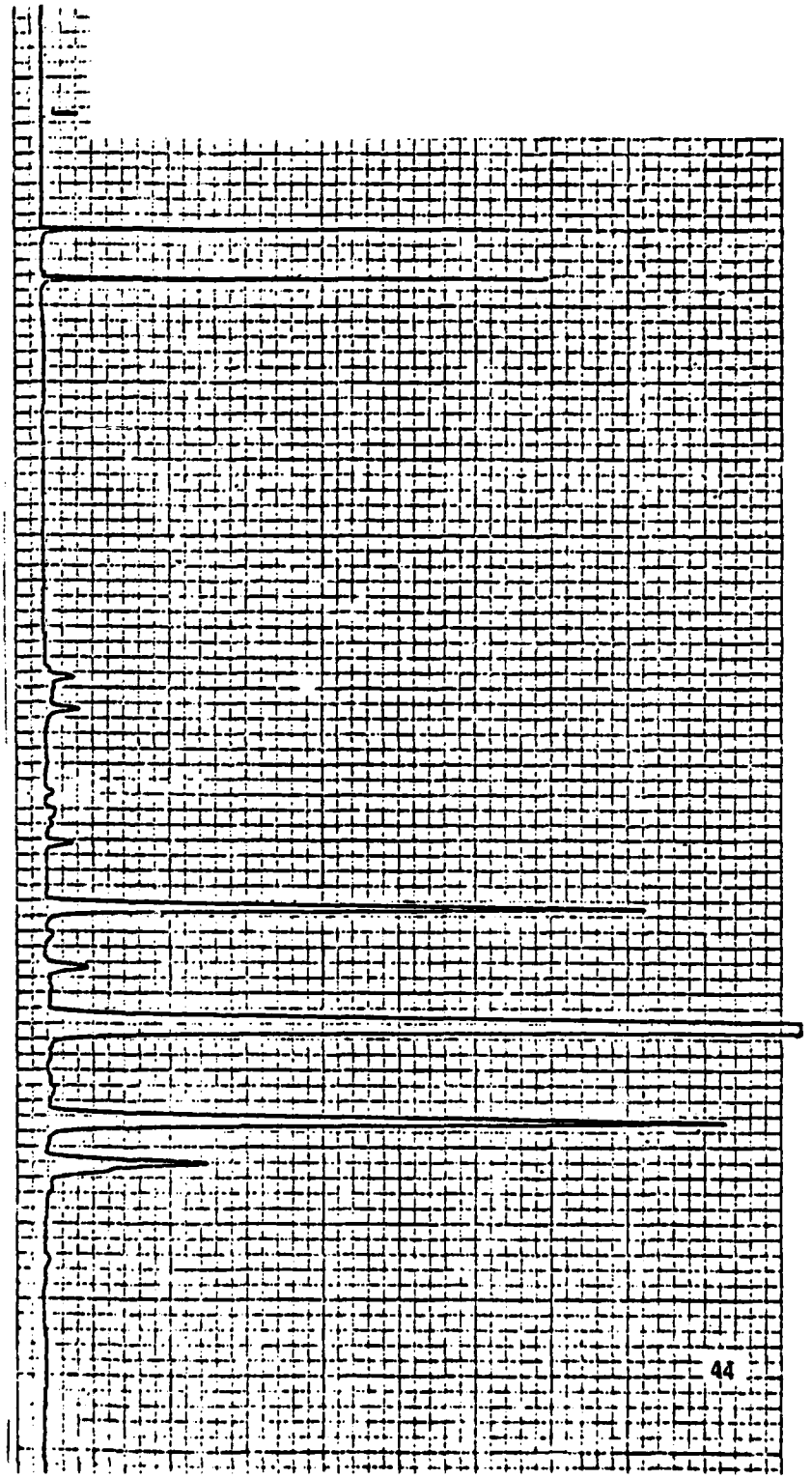


Figure 18

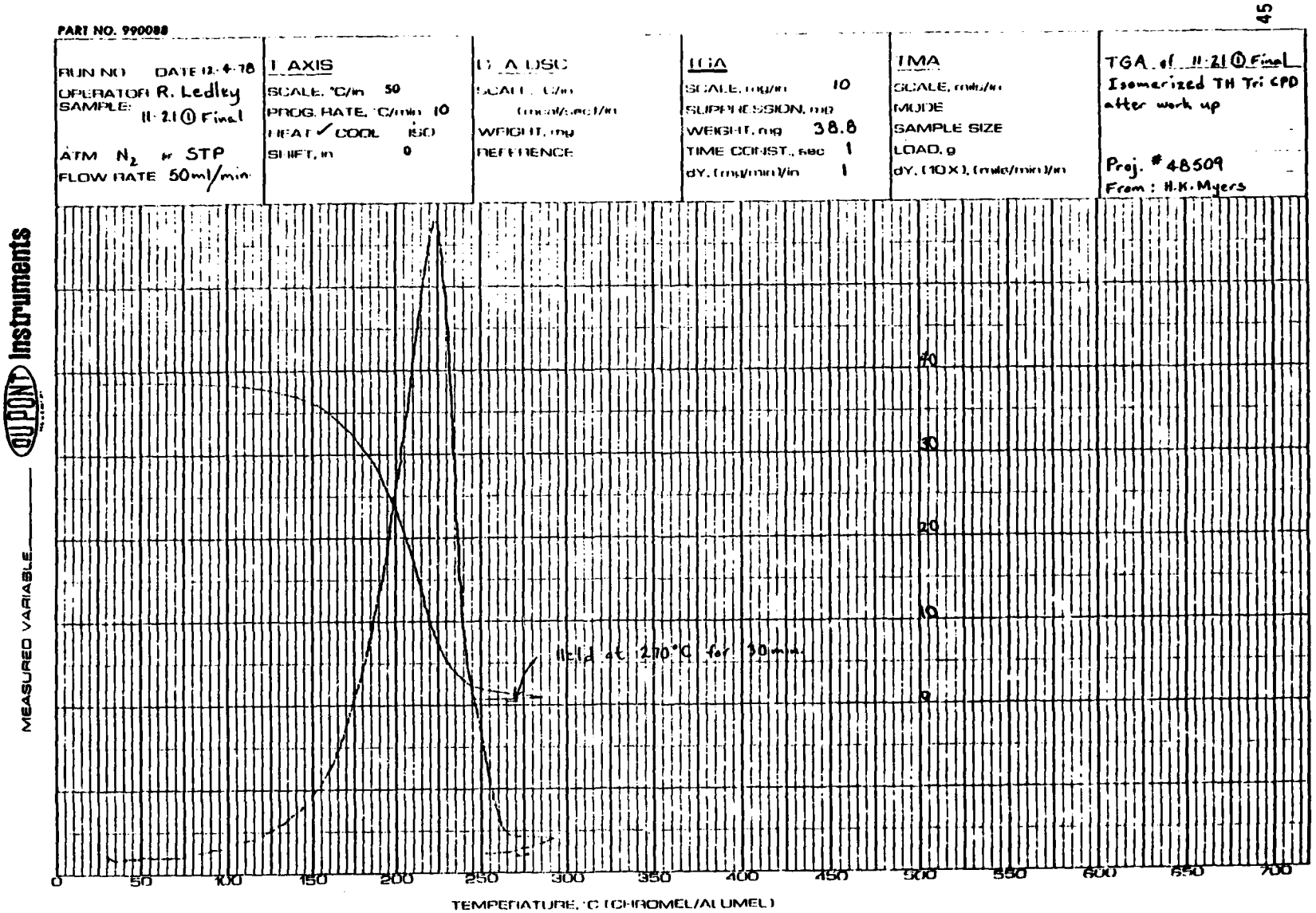
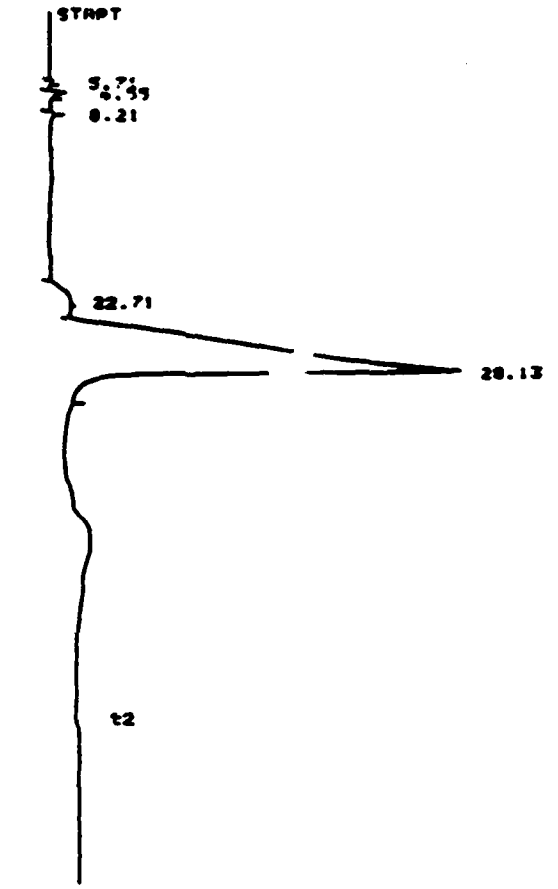

PART NO. 990088
RUN NO DATE 12-4-78
OPERATOR R. Ledley
SAMPLE: II-21① Final
ATM N_2 @ STP
FLOW RATE 50ml/min
I AXIS
SCALE, °C/in 50
PROG. RATE, °C/min 10
HEAT ✓ COOL ISO
SHIFT, in 0
DTA DSC
SCALE, °C/in
(cal/sec)/in
WEIGHT, mg
REFERENCE
TGA
SCALE, mg/in 10
SUPPRESSION, mg
WEIGHT, mg 38.8
TIME CONST., sec 1
dY, (mg/min)/in 1
TMA
SCALE, mils/in
MODE
SAMPLE SIZE
LOAD, g
dY, (10X), (mils/min)/in
TGA of II-21① Final
Isomerized TH Tri CPD
after work up
Proj. # 48509
From: H.K. Myers
MEASURED VARIABLE
DUPONT Instruments
II-21 at 270°C for 30 min.
40
30
20
10
0
0
50
100
150
200
250
300
350
400
450
500
550
600
650
700
TEMPERATURE, °C (CHROMEL/ALUMEL)

Figure 19

NBD-[illegible] from V-7
Charge to Isomerization HKM10-9-78(1)



hp 5830A
AREA %

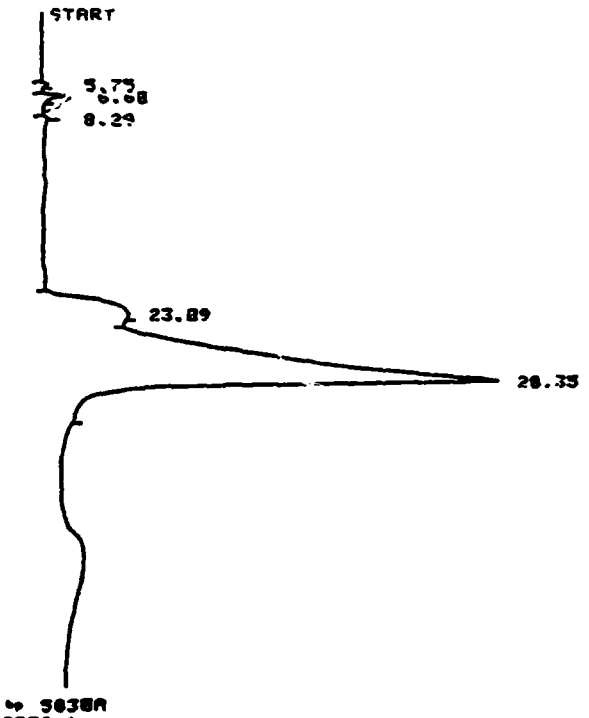
RT	AREA	AREA %
5.71	631	0.098
6.55	3094	0.482
8.21	257	0.040
22.71	6243	0.972
28.13	632388	98.409

XF: 1.0000 E+ 0

TEMP1	141	142
TIME1	27.0	
RATE	10.00	
TEMP2	224	
TIME2	72.0	
INJ TEMP	275	275
TCD TEMP	270	270
AUX TEMP	150	150
OVEN MAX	230	
CHT SPD	0.30	
ATTN 2^	6	
TCD SGNL	A	
SLP SENS	0.07	
AREA REJ	1	
FLOW A	21	
FLOW B	20	
OPTN	3000	
99.0	TEMP2	230

Figure 20

HKM 10-9-78 (1)
160 min. into NN= Isomerization



% 5030A
AREA %

RT	AREA	AREA %
5.73	997	0.159
6.68	4059	0.649
8.29	316	0.051
23.89	29008	4.649
28.35	591888	94.492

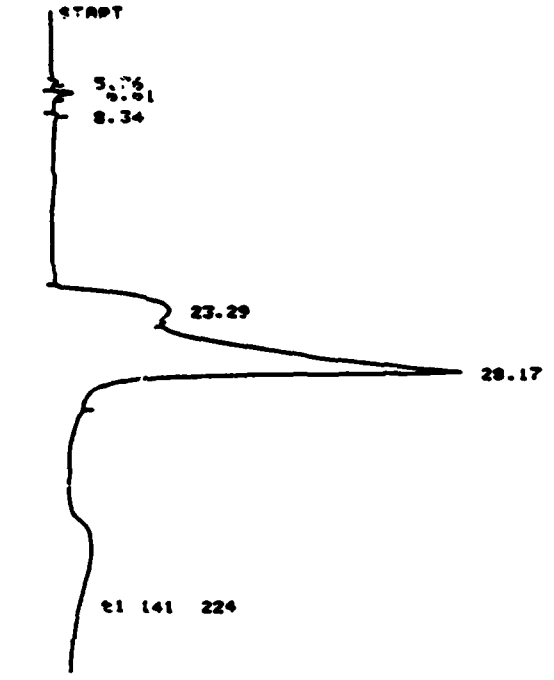
XF: 1.0000 E+ 0

TEMP1	141	177
TIME1	27.0	
RATE	10.00	
TEMP2	224	
TIME2	10.0	
INJ TEMP	275	275
TCD TEMP	270	270
AUX TEMP	150	150
OVEN MAX	230	
CNT %P0	0.30	
ATTN 2^	4	
TCD SGNL	A	
SLP SENS	0.07	
AREA REJ	1	
FLOW A	21	
FLOW B	20	
OPTN	3070	
99.0 TEMP2		230

Figure 21

HKM 10-9-78 (1)

280 min into NN* Isomerization



\~ 5030A
AREA %

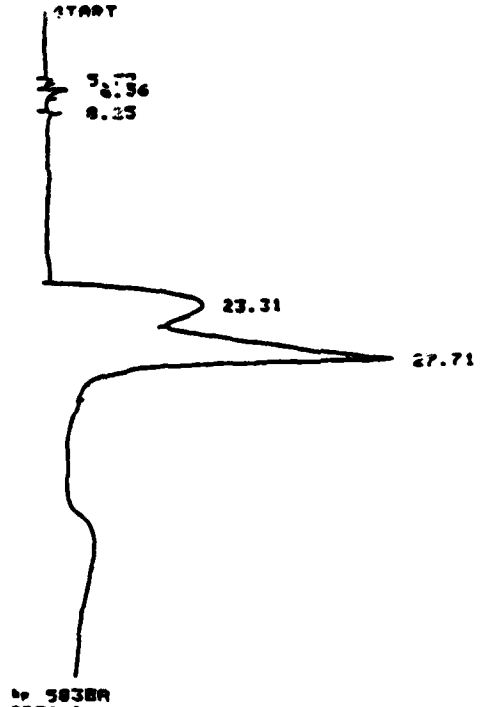
RT	AREA	AREA %
5.76	903	0.196
6.61	4089	0.881
8.34	378	0.074
23.29	67188	13.422
28.17	428038	85.587

XF: 1.0000 E+ 0

TEMP1	141	141
TIME1	27.8	
RATE	18.00	
TEMP2	224	
TIME2	16.8	
INJ TEMP	275	275
TCD TEMP	270	270
AUX TEMP	150	150
OVEN MAX	230	
CHT SPD	0.30	
ATTN 2^	4	
TCD SGNL	A	
SLP SENS	0.07	
AREA REJ	1	
FLOW ^	21	
FLOW B	20	
OPTN	TB%	
55.0	TEMP2	230

Figure 22

HKM 10-9-78 (1)
400 min. into $NN^{=}$ Isomerization



5038A
AREA %

RT	AREA	AREA %
5.72	971	0.128
6.56	4241	0.524
8.25	300	0.038
23.31	280180	35.505
27.71	516888	63.734

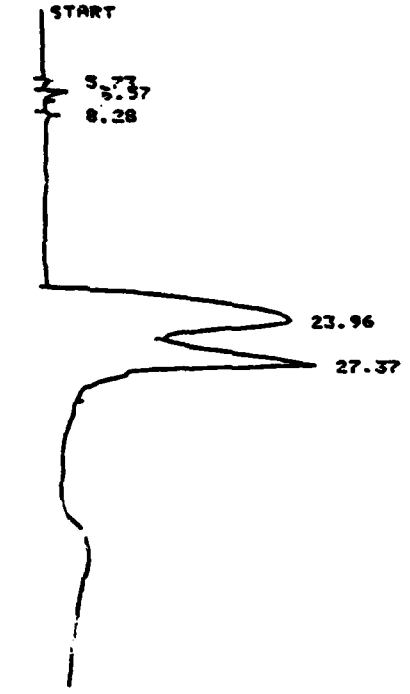
XF: 1.0000 E+ 0

TEMP1	141	141
TIME1	27.0	
RATE	10.00	
TEMP2	230	
TIME2	16.0	
INJ TEMP	275	275
TCD TEMP	270	270
AUX TEMP	150	150
OVEN MAX	230	
CHT SPD	0.30	
ATTN 2↑	6	
TCD SGNL	A	
SLP SENS	0.07	
AREA REJ	1	
FLOW A	21	
FLOW B	21	
OPTN	3090	

Figure 23

HKM 10-9-78 (1)

1465 min into NN* Isomerization



hp 5830A
AREA %

RT	AREA	AREA %
5.73	940	0.117
6.57	4577	0.564
8.29	286	0.035
23.96	462000	56.982
27.37	344400	42.403

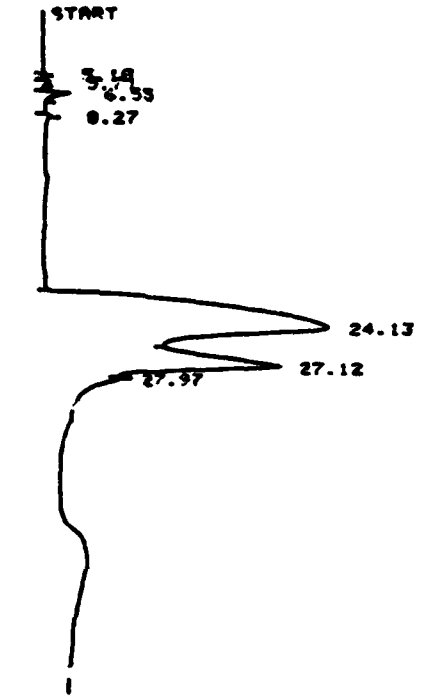
XF: 1.0000 E+ 0

TEMP1	141	141
TIME1	27.0	
RATE	10.00	
TEMP2	230	
TIME2	16.0	
INJ TEMP	275	275
TCD TEMP	270	270
AUX TEMP	150	150
OVEN MAX	230	
CHT SPD	0.30	
ATTN 2+	6	
TCD SGNL	A	
SLP SENS	0.07	
AREA REJ	1	
FLOW A	21	
FLOW B	20	
OPTN	3090	

Figure 24

HKM 10-9-78 (1)

1720 min. into $NN^{=}$ Isomerization



by SCREA
AREA %

RT	AREA	AREA %
5.18	195	0.829
5.71	1849	8.158
6.55	5115	0.778
8.27	345	0.852
24.13	483588	72.831
27.12	173588	26.135
27.97	159	0.824

XF: 1.0000 E+ 0

TEMP1	141	171
TIME1	27.0	
RATE	18.00	
TEMP2	230	
TIME2	16.0	
INJ TEMP	275	275
TCD TEMP	270	270
AUX TEMP	150	150
OVEN MAX	230	
CHT SPD	0.30	
ATTN 2↑	6	
TCD SGNL	A	
SLP SENS	0.07	
APER PEJ	1	
FLOW A	21	
FLOW B	21	
OPTN	3090	

Figure 25

TGA of NN 1790 min. final isomerized sample HKM 10-9-78

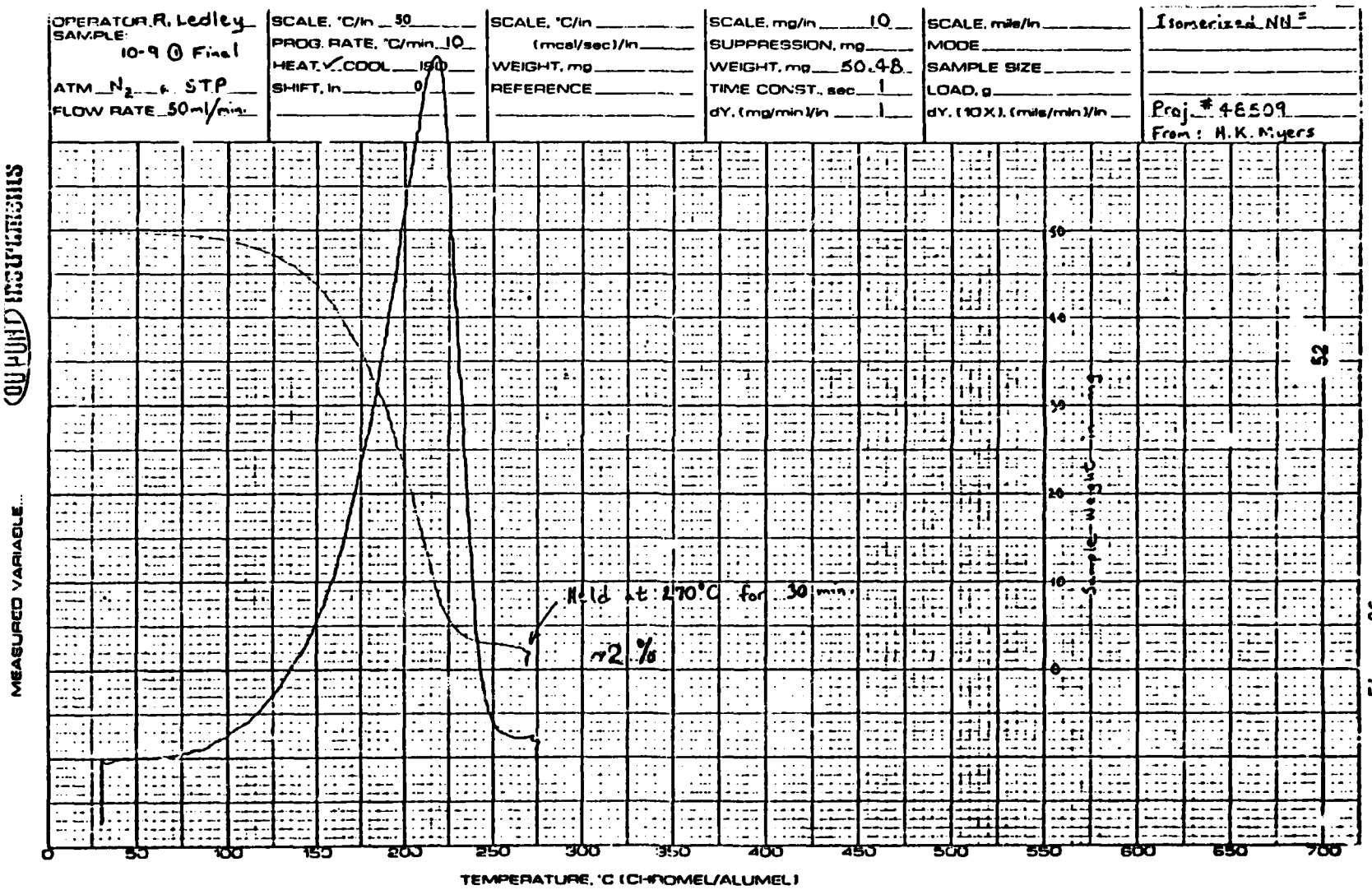


Figure 26

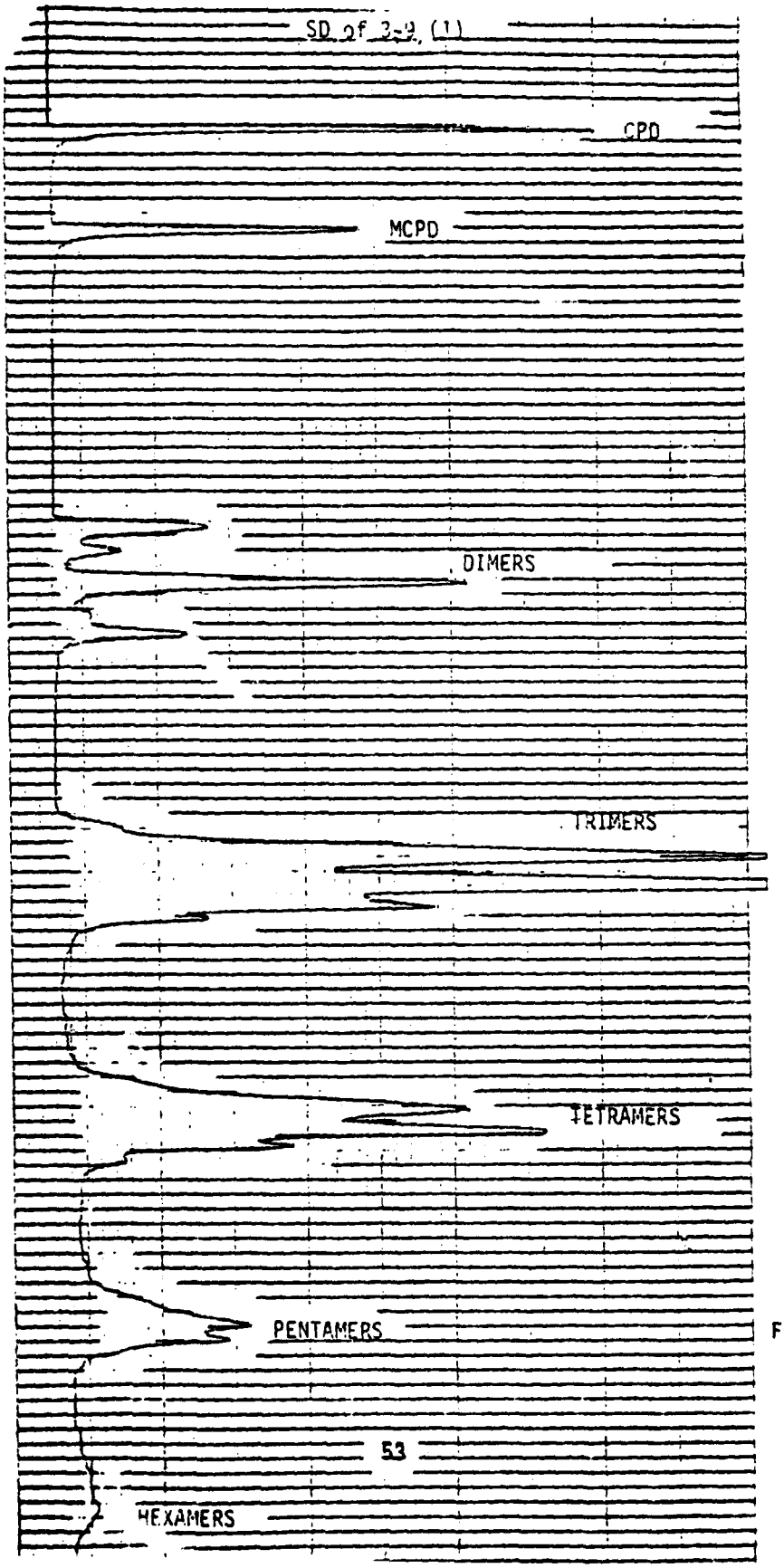

SD of 3-9 (1)
CPD
MCPD
DIMERS
TRIMERS
TETRAMERS
PENTAMERS
HEXAMERS

Figure 27

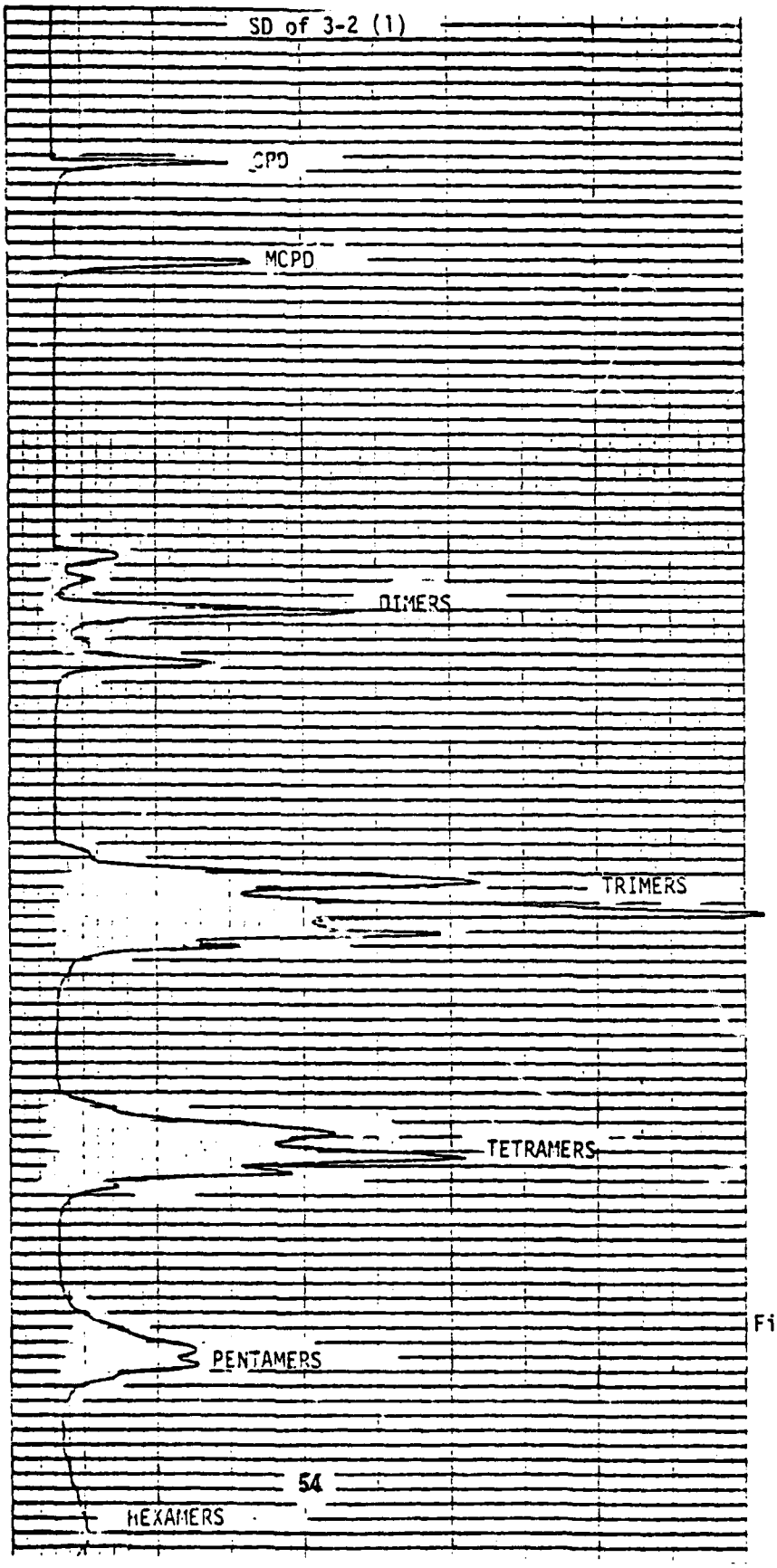

SD of 3-2 (1)
DCPD
MCPD
DIMERS
TRIMERS
TETRAMERS
PENTAMERS
HEXAMERS

Figure 28

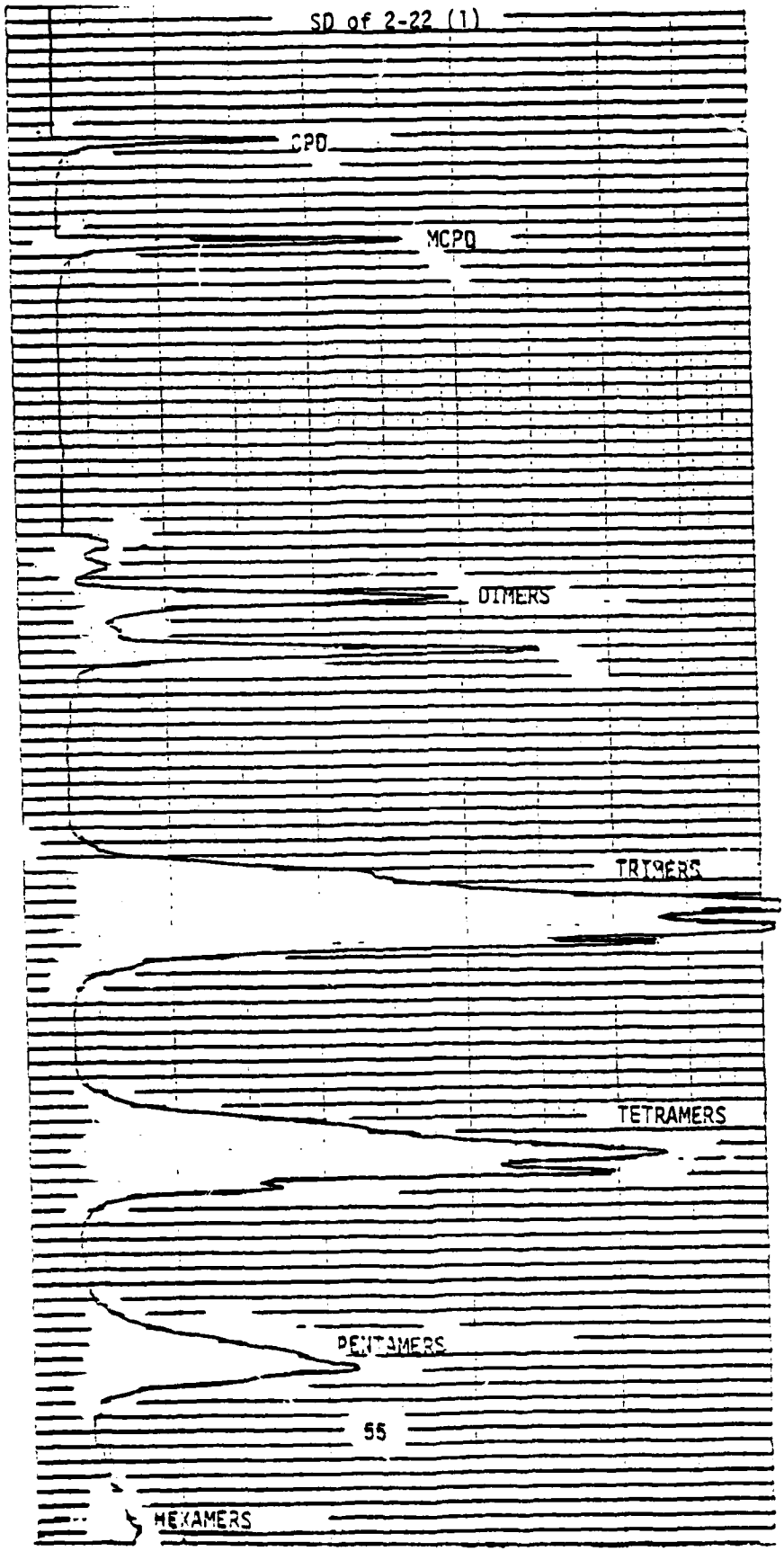

SD of 2-22 (1)
CPD
MCPD
DIMERS
TRIMERS
TETRAMERS
PENTAMERS
HEXAMERS

Figure 29

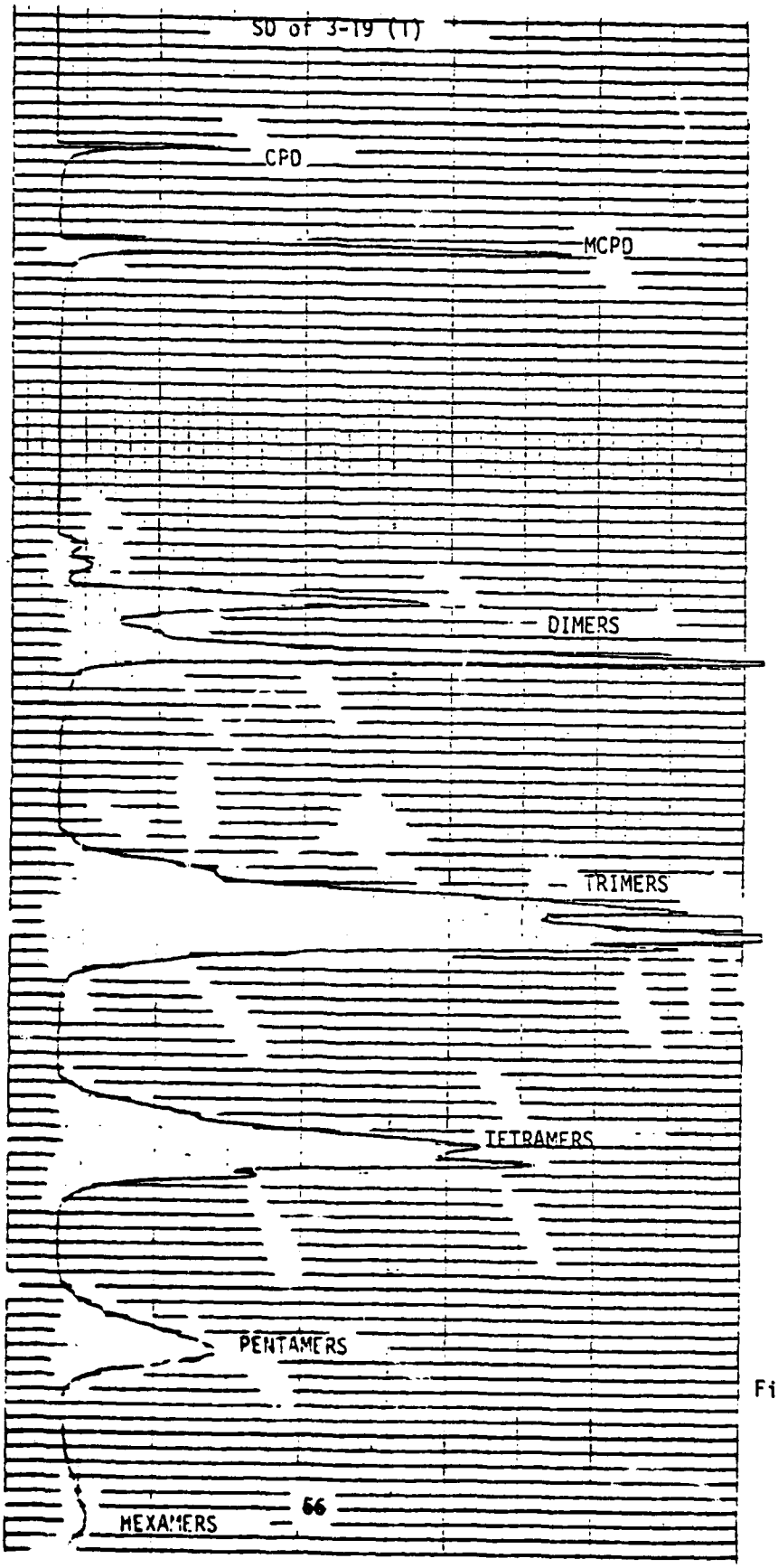

SO of 3-19 (1)
CPD
MCPD
DIMERS
TRIMERS
TETRAMERS
PENTAMERS
HEXAMERS

Figure 30

PART NO. 990088

RUN NO. ___ DATE 9/17/91	T-AXIS	DTA-DSC	TGA	TMA	2-19 D. Final
OPERATOR T. Shaw	SCALE, °C/in 50	SCALE, °C/in	SCALE, mg/in 10	SCALE, mils/in	CPD-MCPD Dimer Oligomers
SAMPLE:	PROG. RATE, °C/min 10	(mcal/sec)/in	SUPPRESSION, mg	MODE	
	HEAT ✓ COOL ___ ISO ___	WEIGHT, mg	WEIGHT, mg 44.87	SAMPLE SIZE	
ATM N_2 @ STP	SHIFT, in 0	REFERENCE	TIME CONST., sec 1	LOAD, g	P.N. 48509
FLOW RATE 50 cc/min			dY, (mg/min)/in 2	dY, (10X), (mils/min)/in	From: M.K. Myers

DUPONT Instruments

MEASURED VARIABLE

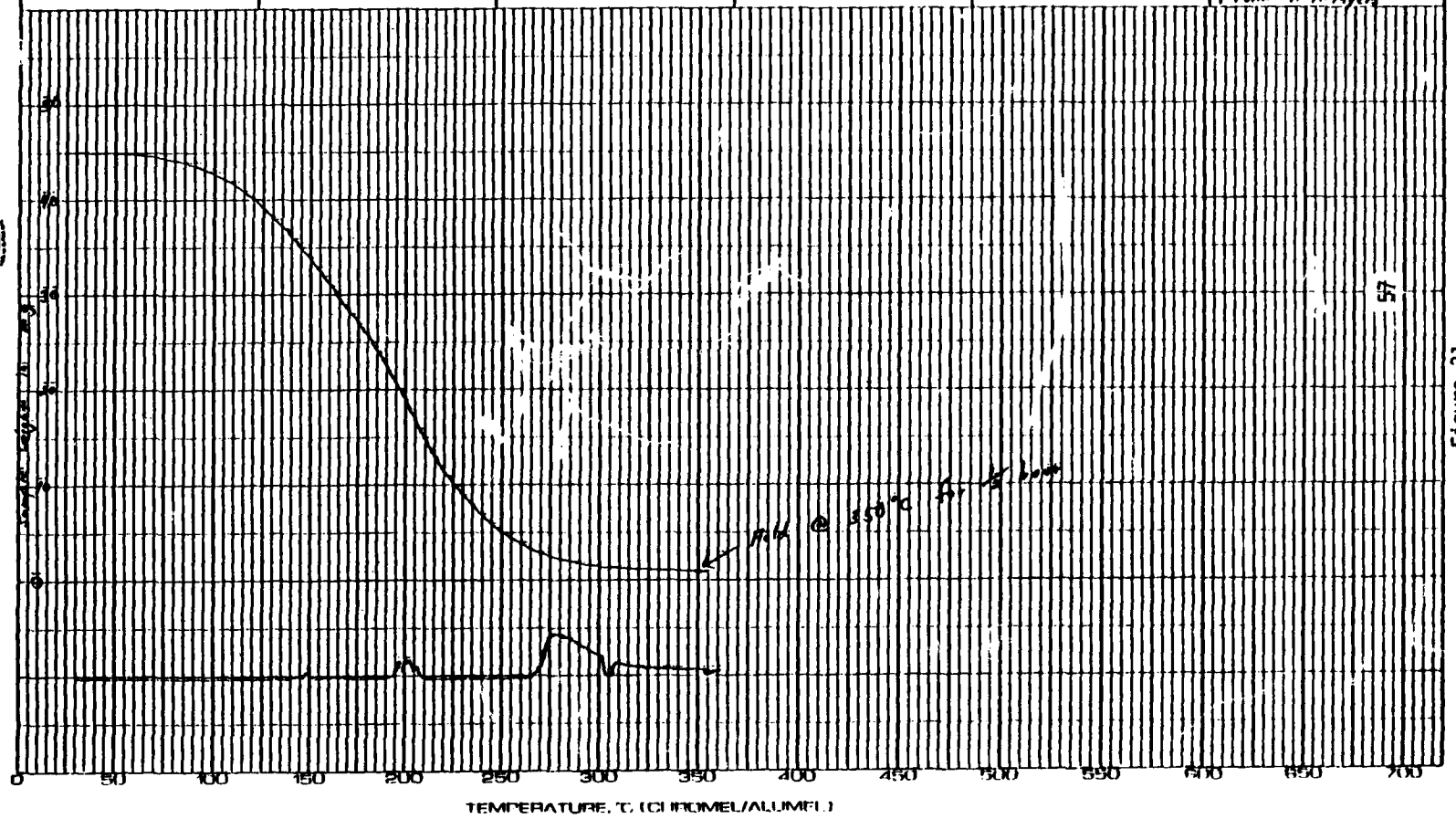


Figure 31

HKM 3-9-79 (1) Cut #4
SD of Isolated Tricyclopentadienes

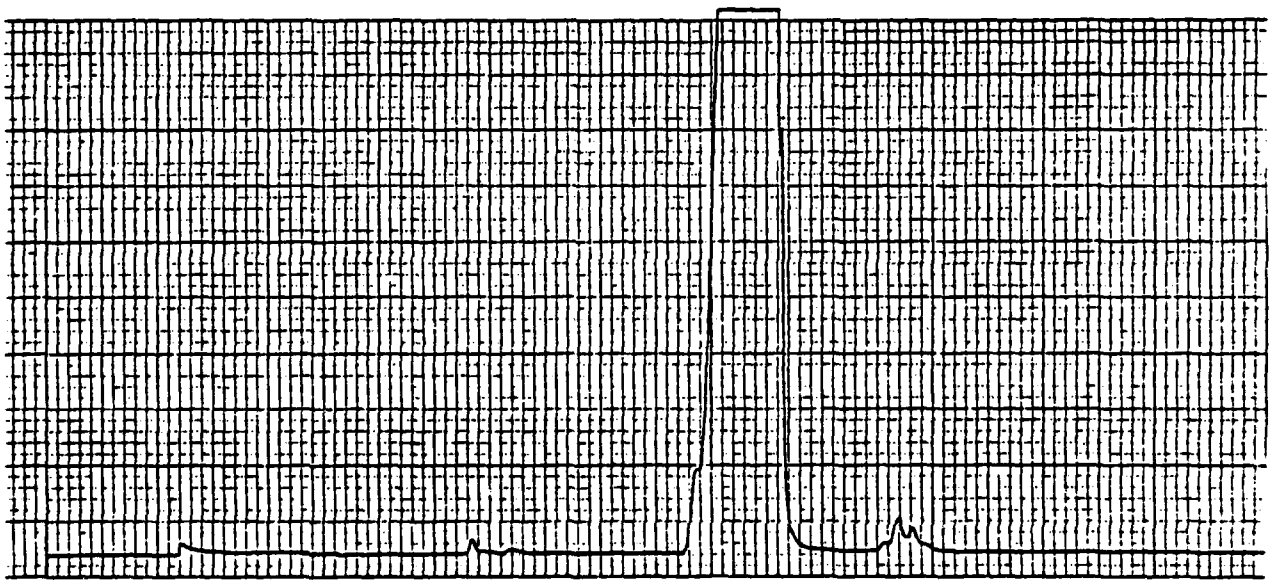


Figure 32

HKM 3-9-79 (1) Cut #7

CPD-MCPD Cooligomers

Decomposition Products

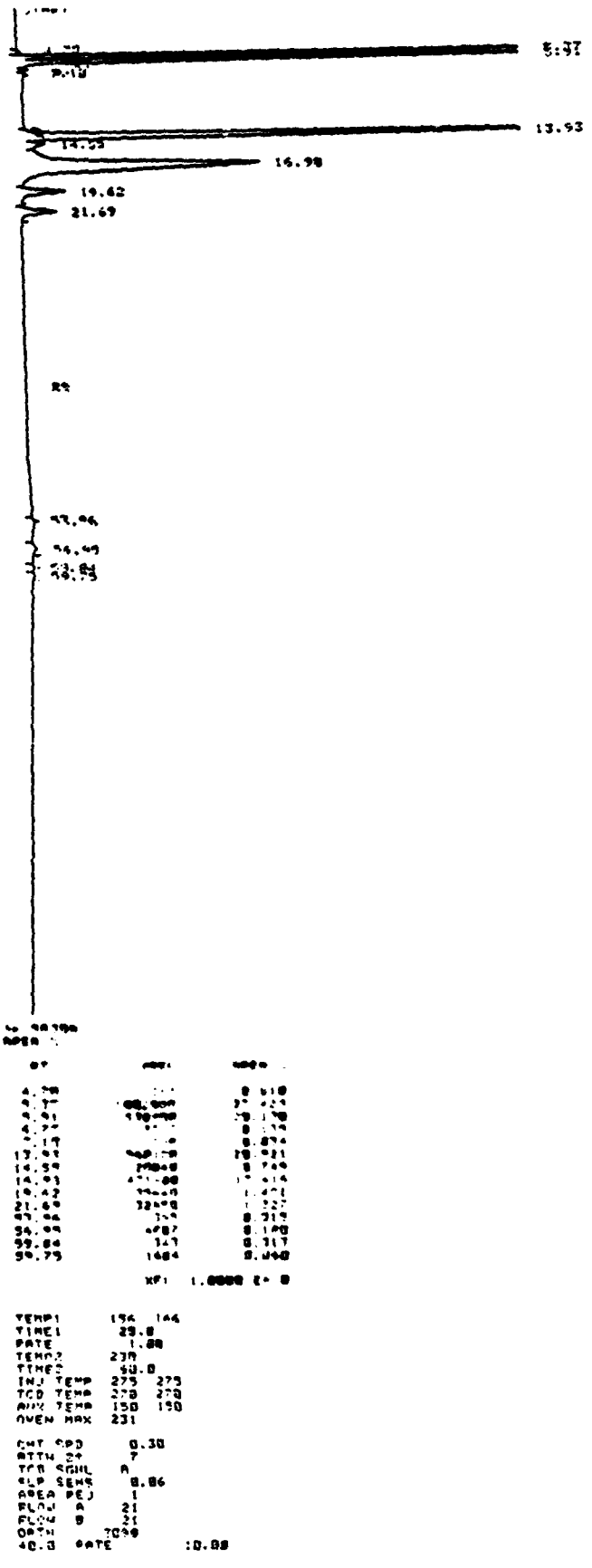


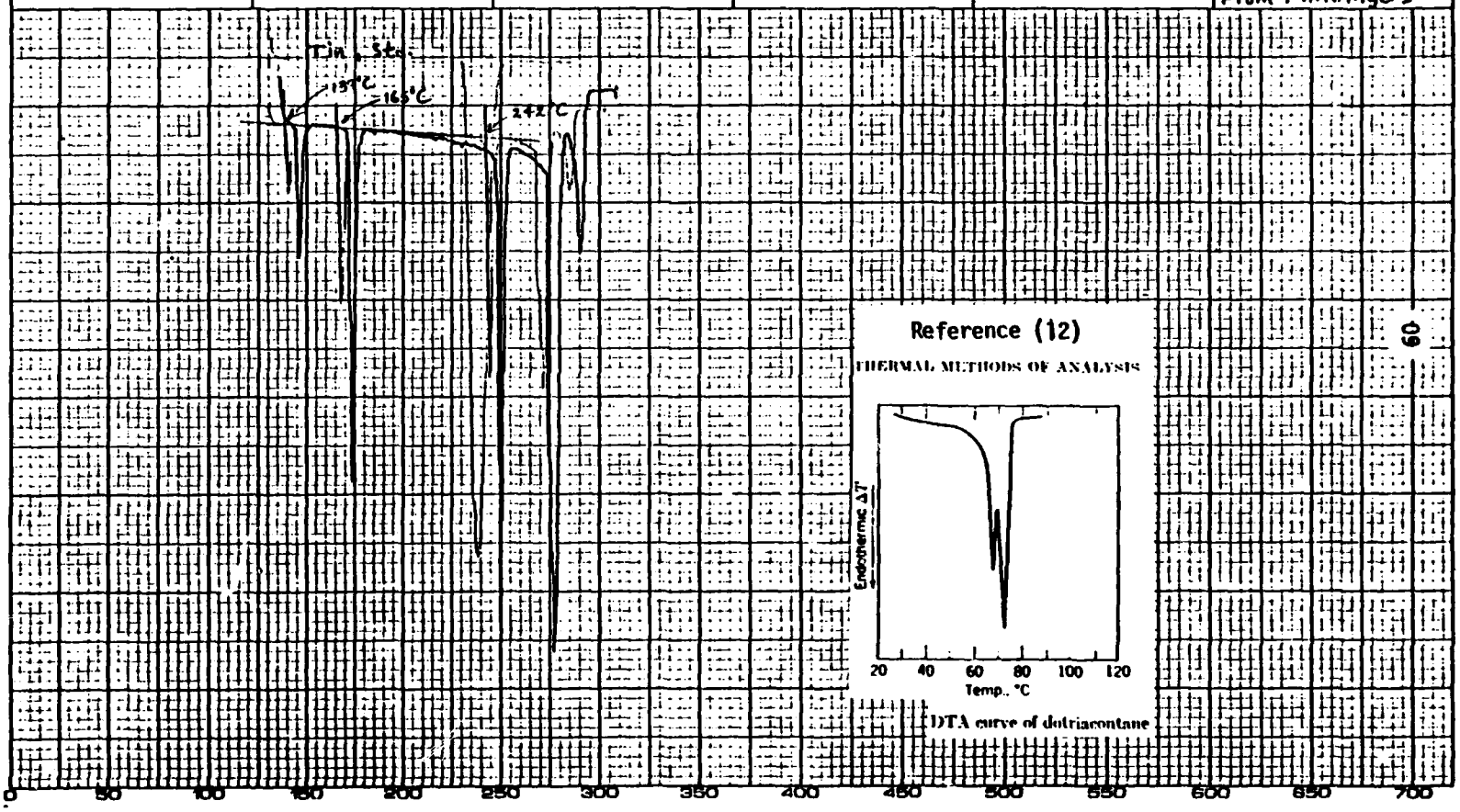
Figure 33

PART NO. 990000

RUN NO ___ DATE 8-25-78	T-AXIS	DTA-DSC	TGA	TMA	DSC of 8-21 ② 1
OPERATOR R. Ledley	SCALE, °C/in 50	SCALE, °C/in	SCALE, mg/in	SCALE, mils/in	Diamantane recrystallized from N_2CCl_4
SAMPLE: 8-21 ② 1	PROG. RATE, °C/min 10	(mcal/sec)/in 1, 2	SUPPRESSION, mg	MODE	
ATM N_2 / p STP	HEAT ✓ COOL ___ ISO ✓	WEIGHT, mg 4.8	WEIGHT, mg	SAMPLE SIZE	
FLOW RATE 50 ml/min	SHIFT, in 0	REFERENCE Empty Pan	TIME CONST., sec	LOAD, g	Proj. # 48509
			dY, (mg/min)/in	dY, (10X), (mils/min)/in	From : H.K. Myers

MEASURED VARIABLE

DUPONT instruments



Reference (12)

THERMAL METHODS OF ANALYSIS

DTA curve of dotriacontane

Figure 34

HKM 4-12-79 (1) Final

S. D. of Cooligomerization of Decomposition Products

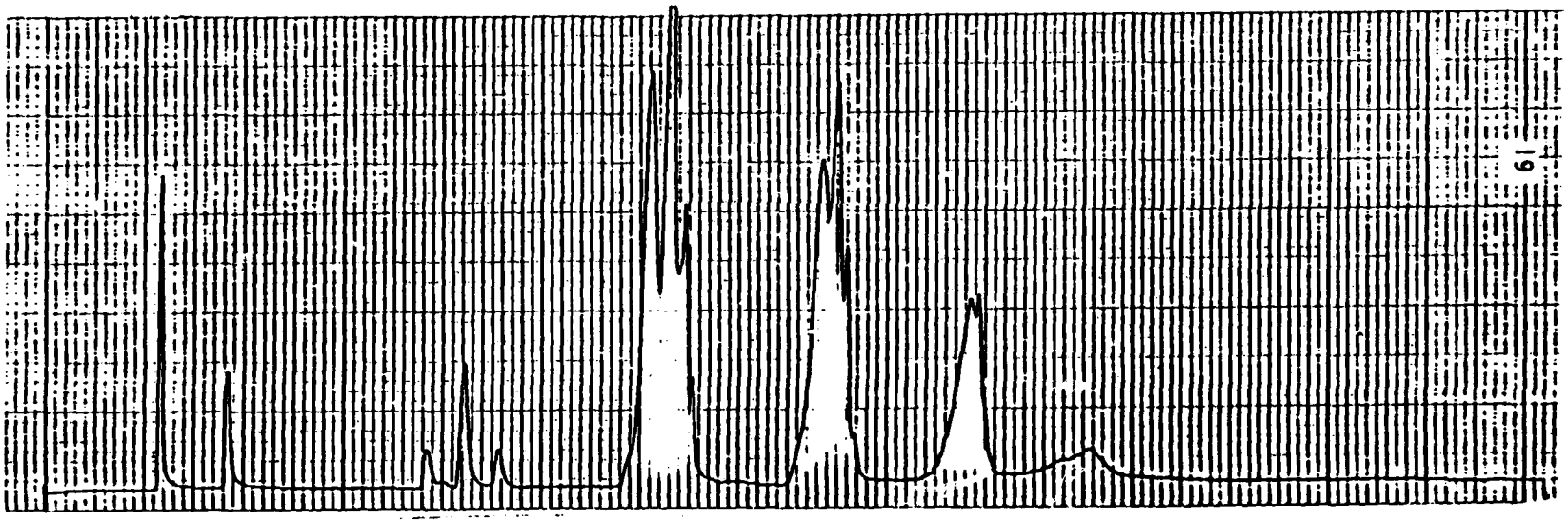


Figure 35

TABLE 1

Binor-S Hydrogenolysis with Rh

7-26 (1) Sample #	Time for T° During Reaction Minutes	T° Range (°C)	Reactor P During Reaction (PSIG)	ΔP of H_2 Reservoir (PSIG)	Absorbed H_2 (Moles)	Required H_2 (Moles)	Binor-S Charge (Moles)
1	100	204-245	390-410	1770-1500 = 270	10.5-8.9 = 1.6	7.6	3.8
2	20	240-249	400	1500-1190 = 310	8.9-7.1 = 1.8		
3	20	245-249	400	1190- 900 = 290	7.1-5.3 = 1.8		
Final	260	225-249	400-419	900- 495 = 405	5.3-2.9 = 2.4		
					7.6		

TABLE 2

Tetrahydro Binor-S H_2SO_4 Wash

Run #	g. THB-S Charge	Washed g. Product	% Yield
HKM 8-4-78(2)	40.0	37.7	94.3
8-21-78(1)	523.5	496.1	94.8
8-24-78(1)	520.4	485.7	93.3
8-28-78(1)	519.0	472.0	90.9

TABLE 3

Reagent Ratios and Products when Isomerizing THB-S to Diamantane with $AlCl_3$

Batch Runs

Run Designation	$AlCl_3$ Parts	$AlCl_3$ Grams	CH_2Cl_2 Parts	CH_2Cl_2 Ml.	Neat THB-S Parts	Neat THB-S Grams	Grams Diamantane Filter Cake	% Conversion
T. Courtney	1	50	50	2500	5.28	264	151	57.2
HKM 8-4(1)	1	7	21.4	150	5.7	40	4.4	61.0
8-7(1)	1	7	21.4	150*	5.7	40	26.8	67.0
8-9(1)	1	5.8	21.6	125	5.7	33.16*	21.5	64.8
8-10(1)	1	14	10.7	150	2.9	40	26.5	66.3
9-3(1)	1	30	13.33	400	12.39	371.8	210.2	56.5
9-7(1)	1	60	6.67	400	5.58	334.9*	212.4	63.4
9-29(1)	1	200	1.5	300	3.0	600	447.9	74.7
Continuous Runs								
8-11(1)	1	11	15.45	170	3.63	40	25.4	63.5
8-16(1)	1	60	8.75	525	3.55	213	132.8	62.3
8-21(2)	1	220	2.95	650	4.4	970*	613	63.2
8-31(1)	1	60.2	6.64	400	6.9	418*	254	60.8

*THB-S charge stock was previously acid washed with concentrated H_2SO_4.

TABLE 4

Diamantane from Binor-S

STEP	REACTION	REAGENTS (a)	TEMP °C	TIME HOURS	WT % STARTING MATERIAL CONVERTED	WT % SELECTIVITY TO DESIRED PROD.
#1	HKM 9-26(1) Hydrogenolysis of Binor-S to tetra-hydro Binor-S (THB-S)	5% Rh/C : 10g Binor-S : 700g H_2 @ 429 psig : 15.2g	260°	5 11	96.8 100	96.55
#2	HKM 1-29(1) Isomerization of tetrahydro Binor-S to "raw" diamantane	$AlCl_3$ (excess) : 200g (b) CH_2Cl_2 : 300 ml THB-S : 600g	65°	5.7 <69.7(c)	<99 100	65.3 74.65
#3	HKM 10-2 (1) Recrystallization of "raw" diamantane	ϕCH_3 : 1500 ml. "raw" diamantane : 392g	111°	<24.(d)	77.35	>99.0

(a) Solvent quantities listed do not include washes of isolated products.
(b) In this example (HKM 9-29 (1)) twice the necessary $AlCl_3$ was used to test this parameter.
(c) Second crop stirred over week-end.
(d) Time to recrystallize is 8 to 24 hours, depending upon the crystal size desired.

TABLE 5

Cyclopentadiene Oligomerization

RUN #	REACTION TIME HOURS	REACTION TEMP. °C	AMBIENT REACTION PRESSURE, PSIG	PRODUCT YIELD GRAMS.
EJJ-743115	7	170 - 200	30 - 60	2568
EJJ-743117	7	170 - 180	20 - 29	2910
EJJ-743119	10	170 - 189	16 - 38	3019
EJJ-743121	10	170 - 185	20 - 36	2903
EJJ-743122	10	170 - 189	28 - 44	2563

TABLE 6

QUANTITATIVE EXAMPLES OF ISOMERIZED THTRICPD PRODUCTION

PROCESS STEP	REACTION #	REAGENT CHARGE					PRODUCT RECOVERED					% YIELD
		Weight	DiCPD		TriCPD		Weight	DiCPD		TriCPD		
		Grams	% (a)	Grams	%	Grams	Grams	%	Grams	% (a)	Grams	
Oligomerization:	EJJ-743115		99				2568					
	743117		99				2910					
	743119		99				3019					
	743121		99				2903					
	743122		99				2563					
DiCPD —170°-200°C, 7-10 Hrs.→ CPD oligomers												
Isolation:	HKM 10-13-78(1) V	2780.9										
	Cut 1						758.9	75.7	574.5	20.9	158.6	
	2						639.9	8.3	53.1	91.0	582.3	
CPD —Distil. @→ TriCPD Oligomers .4mm Hg. to 115°-132°C	3						358.9	1.5	5.38	82.6	296.4	
		(2147.9 non-recyclables=2780.9-633)						(e) 633.			1037.3	37.3
											1037.3	48.3
	HKM 11-9-78(1)	5329.9										
	Cut 1						1008.9	93.0	938	3.2	32.3	
	2						353.9	78.1	276	19.7	69.7	
	3						847.9	28.4	240.8	69.7	591.	
	4						500.	7.5	37.5	91.3	456.5	
	5						233.9	4.3	10.05	94.8	221.7	
	6						223.9	3.0	6.71	96.1	215.2	
	7						149.9	1.1	1.65	82.4	123.5	
	8						235.9	(b) 2.6		82.3	194.1	
								(e) 1510.7			1904.	35.7
		(3819.2 non-recyclables=5329.9-1510.7)									1904.	49.9
Hydrogenation:	HKM 10-27-78(1)	629			91.0	572.4	542			90.4	490	85.6
	11-15-78(1)	494.6			91.3	451.6	451.6			93.1	420.4	93.1
	11-17-78(1)	475.3			(c) 87.8	417.3	429.2			93.0	399.2	95.7
	1-2-79 (1)	687.1			(c) 86.4	593.7	591.6			96.6	571.5	96.3
endo-TriCPD+H_2 —6-8%Ni/K→ endo-THTriCPD @max. 197 psig & 128°-147°C for 2.2-3.4 Hrs.												
Isomerization:	HKM-11-21-78(1)	150			93.0	139.5	101.			96.0	97.0	69.5
	11-29-78(1)	200			90.4	180.8	144.1			90.0	129.7	71.7
	11-30-78(1)	328			90.4	296.5	261.3			91.0	237.8	80.2
endo-TriCPD —9-15% $AlCl_3$ @→ exo-THTriCPD Isomers	12-3-78 (1)	448			93.1	417.1	355.			96.0	340.8	81.7
0°-20°C for 3-9 hrs. saturated with HCl	12-11-78(1)	273			92.0	253.9	205.7			92.1	189.4	74.6
	1-4-79 (1)	590			96.6	569.9	436.3			91.9	401.	70.4
Purification:												
436.3g Decant. from Isom. —Percolated 224°C thru 72g Florisil→ "Raw" THTriCPD Isomers	HKM 1-4-79(1)	436.3			91.9	401.	391.2			91.9	359.5	89.7
"Raw" THTriCPD Isomers —Vac Dist 681°-108°C & .04-.09mm Hg→ Final THTriCPD Isomers	HKM 12-14-78(1)	1041.			(c) 93.2	970.2	825.9			99.	817.4	84.3
	1-9-79 (1)	391.2			91.9	359.5	(d) 162.3			99.	160.7	(d) 44.7

a) Gas chromatographic analysis; (b) Decomposition noticed at end of Cut #7; (c) % TriCPD calculated; (d) Precut still contained 80% THTriCPD

e) CPD dimer may be recyclable.

TABLE 7

CPD-MCPD DIMERS CO(OLIGOMERIZATION

Run #	Dimer Molar Charge			Max. Temp °C	Total Heat. hrs. above 60°C	% Recovery	Final Product Consistency Like:	Simulated Distillation to 440°C						TGA Residue
	CPD	MCPD	Ratio					% Dimers		% Trimers	% Tetramers	% Pentamers	% Hexamers	
								CPD	MCPD					
3-9(1)	10	5	.5	190°	30.2	97.3	Honey	3.2	8.4	42.3	24.2	11.0	3.5	Trace
3-2(1)	7	5	.71	190°	33.	99.4	Honey	1.7	9.5	42.6	25.3	10.9	4.4	3.
2-22(1)	5.5	5.5	1.0	207°	30.4	89.0	Solid wax	1.2	11.8	41.7	25.6	11.1	3.6	Trace
3-19(1)	1.67	3.34	2.0	196°	41.	91.0	SOW Oil	.9	18.6	41.2	22.1	7.7	2.6	Trace

TABLE 8

NN$^{=}$ Isomerization with Alumina at 180°C

Total Reaction Time Minutes	Conversion of NN$^{=}$	% NBD Tetramer
180	10.0	2.1
545	59.3	5.9
965	80.4	6.2

TABLE 9

PROPERTIES

	Binor-S	Diamantane	Isom. $NN^{=}$	Isom. $NN^{=}$ $+H_2$	Isom. THTriCPD
Structure	Heptacyclic	Pentacyclic	Hexacyclic	Hexacyclic	Pentacyclic
Molecular Formula	$C_{14}H_{16}$	$C_{14}H_{20}$	$C_{14}H_{16}$	$C_{14}H_{18}$	$C_{15}H_{18}$
Mole Wt.	184	188	184	186	202
Melt Pt. (if solid)	66°	244°		-18	
Boil Pt. (if liquid)				270° (est.)	340°
Sp. Gr.	1.131 @ 60°F	1.21	1.1237 (64%)*	1.1095 (77%)*	1.0376
ΔH comb., Net., BTU/gal.	170,000	167,023		163,606	155,522
Viscosity @ 0°F (if liquid)				166.2 cst	
@ 77°F					26.8 cst
@ 100°F				13.9 cst	16.32 cst
Ref.			HKM 12/7 (2)	HKM 4/13 (1) 12/16/77 (1) 3/21 (2)	HKM 12/14/78 (1)

*% Purity

CHART 1 DISTILLATION OF BINOR-S

TBP DISTILLATION ANALYSIS
AND ANALYTICAL
OPERATIONS
FROM R.A.ERSEK D-147 EXT. 5229

PROJECT NUMBER	DATE	SAMPLE NUMBER	DESCRIPTION OF SAMPLE	SIZE (MLS.)	SUBMITTED BY	NOTEBOOK PAGE NO.
68-509	6-20-78	P-52-6869	BINOR-S	11900	J.TICE	778307

CUT #	TEMP.	WT. GMS.	VOL. MLS.	SP.GR.60/60 F	WT.PCT.	VOL.PCT.
	402		0		0.0	0.0
	505		100		0.7	0.9
1	505	899.9		0.8459	0.7	0.9
	505		400		3.9	4.3
2	505	432.9		1.0999	3.2	3.3
	512		600		8.1	9.2
3	512	659.9		1.1291	4.9	4.9
	512		600		13.9	14.2
4	512	668.9		1.1282	5.0	5.0
	512		600		18.9	19.2
5	512	661.9		1.1322	4.9	4.9
	512		600		23.9	24.1
6	512	661.9		1.1296	4.9	4.9
	513		600		28.9	29.1
7	513	668.9		1.1301	5.0	5.0
	514		600		33.9	34.1
8	514	668.9		1.1305	5.0	5.0
	514		650		39.4	39.6
9	514	732.9		1.1310	5.4	5.4
	514		600		44.4	44.6
10	514	667.9		1.1310	5.0	4.9
	514		600		49.4	49.6
11	514	664.9		1.1310	4.9	4.9
	514		900		56.8	56.9
12	514	984.9		1.1310	7.3	7.3
	514		900		64.2	64.3
13	514	985.9		1.1310	7.3	7.3
	514		900		71.5	71.6
14	514	981.9		1.1310	7.3	7.3
	514		900		79.0	79.0
15	514	989.9		1.1310	7.4	7.3
	514		900		86.4	86.5
16	514	991.9		1.1310	7.4	7.4
	514		900		93.8	93.9
17	514	990.9		1.1310	7.4	7.4
	527		500		98.0	98.0
18	527	556.9		1.1310	4.1	4.1
	527		200		99.8	99.8
19	527	238.9		1.1269	1.7	1.7
20	527	17.9		1.1310	0.1	0.1
	TOTAL	13329.9		1.1267		
	CHARGE	13329.9		1.1249	100.0	100.0
	LOSS	0.0				

Chart 2. Mass Analysis
of Sample No. 1. HKM 6-23-78(1) Method 06

PROCEED
CALLING PROGRAM CALPT-MAX. NO. OF PEAKS=300

M.S. NUMBER = 420

MASS	PATT	DIV										
76	0.8	1.	134	1.6	2.	206	3.0	5.	357	3.3	5.	
77	0.7	1.	136	0.7	1.	209	3.0	5.	359	3.2	5.	
78	0.9	1.	137	0.9	1.	214	3.0	5.	367	3.6	5.	
79	0.9	1.	141	1.0	1.	222	3.1	5.	370	3.2	5.	
80	1.9	3.	142	0.7	1.	223	3.3	5.	373	2.8	4.	
81	1.5	2.	143	2.5	4.	224	3.0	5.	374	3.5	5.	
84	0.6	0.	144	4.0	6.	226	4.7	7.	376	2.3	4.	
86	0.9	1.	145	7.1	11.	227	2.9	4.	377	3.6	5.	
87	0.9	1.	146	5.5	9.	229	3.4	5.	378	5.5	9.	
88	0.7	1.	147	1.9	3.	235	3.3	5.	379	3.0	5.	
90	0.8	1.	148	0.7	1.	237	3.3	5.	381	3.1	5.	
92	1.0	2.	151	0.7	1.	240	3.1	5.	382	2.6	4.	
94	2.0	3.	154	2.5	4.	243	3.3	5.	383	3.2	5.	
95	2.5	4.	155	0.4	0.	257	5.7	9.	385	3.1	5.	
98	0.6	0.	157	9.5	15.	259	3.4	5.	390	3.3	5.	
100	0.9	1.	158	11.9	19.	260	2.8	4.	404	3.1	5.	
101	3.3	1.	159	5.5	9.	261	3.1	5.	406	2.7	4.	
103	3.6	5.	160	4.1	6.	264	2.7	4.	407	3.1	5.	
104	4.8	7.	161	3.0	5.	273	4.0	6.	408	3.1	5.	
105	3.9	6.	164	3.4	5.	276	3.0	5.	410	2.7	4.	
107	2.5	4.	166	3.1	5.	281	3.7	6.	414	3.0	5.	
108	3.6	6.	168	3.2	5.	282	3.0	5.	427	2.7	4.	
109	0.5	0.	169	2.7	4.	286	3.0	5.	434	2.9	4.	
114	0.6	0.	171	4.8	8.	287	3.0	5.	437	3.0	5.	
115	3.2	5.	173	4.0	6.	296	2.6	4.	440	4.8	7.	
116	1.6	2.	174	3.0	5.	300	3.0	5.	444	2.9	4.	
117	2.7	4.	176	3.2	5.	306	3.1	5.	455	2.8	4.	
118	7.5	12.	178	3.1	5.	307	3.0	5.	459	3.1	5.	
119	2.4	3.	179	3.0	5.	310	4.8	8.	463	3.3	5.	
120	2.8	4.	180	3.6	6.	314	3.5	5.	467	3.3	5.	
121	0.8	1.	186	100.0	166.	315	2.9	4.	468	3.3	5.	
123	0.5	0.	187	18.2	30.	323	3.0	5.	472	2.8	4.	
124	0.8	1.	188	50.4	83.	329	3.3	5.	474	3.6	5.	
125	0.9	1.	189	10.2	16.	332	2.9	4.	477	3.0	5.	
126	0.4	0.	190	5.2	8.	336	3.0	5.	481	3.1	5.	
128	0.6	1.	194	2.8	4.	337	3.0	5.	484	3.4	5.	
129	3.4	5.	195	3.1	5.	338	3.3	5.	489	3.1	5.	
130	4.5	7.	196	2.6	4.	341	3.0	5.	491	3.1	5.	
131	4.1	6.	197	4.9	8.	345	3.0	5.	495	3.3	5.	
134	3.1	5.	199	3.1	5.	348	2.7	4.	496	3.6	5.	
135	2.0	3.	200	4.2	6.	350	3.6	5.	497	3.3	5.	
								1	501	3.1	5.	

[redacted] CALPT TRANSFORMS ANALOG DATA IN THE FORM OF PEAKS INTO A DIGITAL FORM
[redacted] THE LARGEST PEAK AS 100. PERCENT AND DIVIDING IT INTO ALL THE OTHER PEAKS
[redacted] IS NOT AN ANALYSIS

Chart 3. Mass Analysis
of Sample No. 2. HKM 6-23-78(1)

PROCEED
CALLING PROGRAM CALPT-MAX. NO. OF PEAKS=300
M.S. NUMBER = 427

MASS	PATT	DIV									
78	1.0	1.	134	2.7	4.	234	0.6	1.	353	0.6	1.
80	1.3	2.	137	0.6	1.	250	1.0	1.	359	0.6	1.
81	1.1	1.	138	0.5	0.	253	1.0	1.	362	0.8	0.
82	0.6	0.	140	0.5	0.	256	0.6	0.	370	1.7	2.
84	0.8	1.	143	1.9	3.	259	0.7	1.	371	0.9	1.
85	0.9	1.	144	2.5	3.	261	0.7	1.	382	0.6	0.
87	0.5	0.	145	10.4	16.	265	1.1	1.	384	0.8	1.
91	0.9	1.	146	9.7	15.	266	0.5	0.	393	1.1	1.
92	1.7	2.	147	4.1	6.	271	0.9	1.	395	1.0	1.
94	1.0	2.	148	3.9	6.	275	0.6	0.	406	0.6	0.
95	1.8	2.	150	0.7	1.	283	1.0	1.	411	0.8	1.
96	1.0	1.	151	1.4	2.	291	1.2	1.	415	0.6	1.
97	1.2	1.	157	5.7	8.	296	1.0	1.	418	0.5	0.
98	0.6	0.	158	7.6	11.	298	0.7	1.	421	1.7	2.
104	2.0	4.	159	3.0	5.	301	1.0	1.	430	3.1	5.
105	0.8	1.	160	2.4	3.	302	0.6	0.	431	0.8	1.
106	2.2	3.	169	0.7	1.	303	0.4	0.	432	1.2	1.
107	1.1	1.	171	1.5	2.	305	0.9	1.	442	0.7	1.
108	2.8	4.	173	3.3	5.	306	0.6	0.	445	1.0	1.
109	1.1	1.	174	0.6	0.	311	1.0	1.	449	1.0	1.
110	1.3	2.	182	0.5	0.	314	1.0	1.	453	0.9	1.
111	0.3	0.	186	35.1	134.	316	1.4	2.	456	0.8	1.
112	0.6	1.	187	13.9	21.	318	3.0	4.	463	0.7	1.
113	0.8	1.	188	100.0	157.	320	0.6	1.	466	1.1	1.
117	0.7	1.	189	14.2	22.	321	1.6	2.	469	0.6	0.
118	1.3	2.	190	3.6	5.	322	2.6	4.	473	0.7	1.
119	1.5	2.	198	3.1	4.	324	1.3	2.	474	0.6	1.
120	1.3	2.	201	1.0	1.	326	1.4	2.	475	0.7	1.
121	1.1	1.	204	0.5	0.	332	0.6	1.	477	0.9	1.
125	2.3	3.	206	0.8	1.	333	0.8	1.	479	0.5	0.
128	0.4	0.	208	0.8	1.	334	0.7	1.	480	0.7	1.
129	1.2	1.	220	0.7	1.	339	0.8	1.	481	1.1	1.
130	2.9	4.	223	0.5	0.	340	3.4	5.	485	0.6	1.
131	4.8	7.	224	0.9	1.	343	0.7	1.	491	1.2	1.
132	3.6	5.	226	0.5	0.	346	0.8	1.	495	0.9	1.
133	2.2	3.	252	1.2	1.	352	0.8	1.	497	0.6	1.
									498	0.6	0.

PROGRAM CALPT TRANSFORMS ANALOG DATA IN THE FORM OF PEAKS INTO A DIGITAL FORM BY SETTING THE LARGEST PEAK AS 100. PERCENT AND DIVIDING IT INTO ALL THE OTHER PEAKS. THIS DATA LISTING IS NOT AN ANALYSIS

Chart 4. Mass Analysis
of Sample No. 3. HKM 6-23-78(1)

PROCEED
CALLING PROGRAM CALPT-MAX. NO. OF PEAKS=300
M.S. NUMBER = 428

MASS	PATT	DIV											
76	0.2	0.	146	7.9	19.	213	0.4	1.	382	0.2	0.
78	0.6	1.	147	3.2	7.	215	0.7	1.	383	1.0	2.
79	0.8	1.	148	1.0	2.	216	0.6	1.	385	0.6	1.
80	0.6	1.	149	0.4	1.	217	0.6	1.	386	0.5	1.
81	0.6	1.	150	0.3	0.	218	0.4	1.	390	0.9	2.
82	0.6	1.	151	0.4	1.	219	0.6	1.	392	0.4	0.
83	0.7	1.	152	0.4	1.	220	0.4	0.	393	0.5	1.
85	0.6	1.	153	0.9	2.	223	0.6	1.	399	0.8	1.
86	0.6	1.	154	0.7	1.	230	0.5	1.	403	0.7	1.
87	0.7	1.	155	0.6	1.	232	0.4	1.	413	0.7	1.
88	0.8	2.	156	0.6	1.	242	0.4	0.	414	0.5	1.
89	0.7	1.	157	1.5	3.	246	0.4	1.	417	0.4	0.
90	0.5	1.	158	0.9	2.	257	0.4	0.	420	0.5	1.
91	0.4	1.	159	2.2	5.	258	0.4	1.	422	0.4	1.
92	1.2	3.	160	2.6	6.	260	0.4	1.	424	0.3	0.
94	0.6	2.	161	1.2	3.	263	0.4	1.	425	0.5	1.
95	0.6	1.	162	0.4	1.	266	0.5	1.	427	0.5	1.
99	0.5	1.	165	0.7	1.	278	0.4	1.	431	0.5	1.
102	0.9	2.	168	0.4	1.	279	0.9	2.	436	0.7	1.
103	0.7	1.	171	0.2	0.	300	0.3	0.	438	0.9	2.
105	0.4	1.	173	3.0	7.	305	0.4	0.	447	1.0	2.
107	0.5	1.	174	0.4	0.	311	0.6	1.	448	0.6	1.
108	1.3	3.	175	0.7	1.	313	0.4	1.	449	0.8	2.
109	0.6	1.	177	0.4	1.	315	0.6	1.	451	0.3	0.
110	1.3	3.	178	0.4	1.	333	0.5	1.	455	0.6	1.
114	0.5	1.	182	0.4	1.	335	0.4	0.	456	0.5	1.
116	0.4	1.	184	0.4	1.	336	0.6	1.	460	0.5	1.
118	0.5	1.	186	26.7	65.	344	0.4	0.	461	0.6	1.
120	1.3	3.	187	5.0	12.	345	0.4	0.	465	0.3	0.
121	0.6	1.	188	100.0	244.	346	0.5	1.	471	0.5	1.
123	0.3	0.	189	14.7	36.	348	0.5	1.	474	0.5	1.
129	0.4	1.	190	3.1	7.	352	0.4	1.	476	0.4	1.
131	3.0	7.	191	0.6	1.	354	0.6	1.	483	0.4	1.
132	2.2	5.	192	0.6	1.	357	0.5	1.	484	1.1	2.
133	1.5	3.	193	0.5	1.	358	0.6	1.	486	0.4	1.
134	2.1	5.	196	0.4	1.	360	0.4	1.	488	0.4	1.
135	0.6	1.	197	0.5	1.	365	0.4	1.	494	0.5	1.
136	0.6	1.	200	0.7	1.	370	0.4	1.	495	0.4	1.
137	0.6	1.	202	0.4	1.	373	0.4	1.	496	0.6	1.
138	0.5	1.	206	0.2	0.	376	0.9	2.	497	0.6	1.
140	0.8	2.	210	0.8	2.	379	0.2	0.	499	0.8	1.
145	8.5	20.	211	0.6	1.	381	0.6	1.	500	0.6	1.

PROGRAM CALPT TRANSFORMS ANALOG DATA IN THE FORM OF PEAKS INTO A DIGITAL FORM BY SETTING THE LARGEST PEAK AS 100. PERCENT AND DIVIDING IT INTO ALL THE OTHER PEAKS THIS DATA LISTING IS NOT AN ANALYSIS

CHART #5

Simulated Distillation of EJJ743117 CPD

CALIBRATION 2 Oligomers

CUT POINT	TIME	DEGREES F	SIM VBR*
IBP	148.	117.0	261.0
5	148.	117.0	261.0
10	148.	117.0	261.0
15	450.	328.7	430.6
20	464.	338.2	438.2
25	464.	338.2	438.2
30	471.	343.0	442.0
35	471.	343.0	442.0
40	471.	343.0	442.0
45	692.	497.9	566.1
50	708.	509.1	575.1
55	708.	509.1	575.1
60	716.	514.8	579.6
65	716.	514.8	579.6
70	725.	521.2	584.8
75	725.	521.2	584.8
80	866.	619.7	663.7
85	898.	642.2	681.7
90	910.	650.0	688.0
95	1054.	751.0	768.9
FBP	1423.	1009.6	908.7

* FROM EXPERIMENTAL CORRELATION 8/16/77
IGNORE IF INITIAL IS LESS THAN 450 F

THIS SD ASSUMES THAT THE WHOLE SAMPLE VAPORIZED

SUNTECH AND ANALYTICAL SERVICES-GC ANALYSIS

DIGITIZER RUN - INST. NO. 14 JOB NO. 18

ELUTION TIME (SEC)	CUM AREA PCT	AREA PCT
137.3	0.000	0.000
148.4	14.010	14.010
181.7	16.398	2.387
188.7	16.541	0.143
206.3	16.578	0.036
211.7	16.624	0.046
220.4	16.658	0.033
229.4	16.703	0.045
237.1	16.716	0.012
240.3	16.764	0.048
256.6	16.812	0.048
270.8	16.818	0.006
279.8	16.835	0.017
282.7	16.846	0.010
290.6	16.868	0.021
305.1	16.876	0.008
317.1	16.880	0.003
323.1	16.883	0.003
328.8	16.886	0.002
393.7	16.887	0.001
429.3	16.898	0.010
461.5	16.924	0.026
480.8	17.427	0.503
484.4	25.251	10.824
471.3	41.409	16.157
498.4	41.581	0.172
502.4	41.680	0.128
523.4	41.720	0.040
539.5	41.732	0.012
550.2	41.738	0.006
591.1	41.751	0.014
602.9	41.752	0.001
644.7	41.772	0.019
664.3	41.796	0.027
684.4	43.883	2.087
692.6	45.027	1.175
708.8	57.460	12.432
715.7	58.589	1.129
725.3	71.173	12.584
767.9	71.417	0.244
773.1	71.432	0.015
776.6	71.451	0.019
781.3	71.468	0.016
786.7	71.485	0.017
794.1	71.496	0.009
803.6	71.557	0.061
819.4	71.567	0.009
826.4	71.600	0.033
842.3	71.623	0.023
846.6	71.640	0.016
866.6	80.122	8.481
885.5	83.864	3.741
894.3	86.338	2.383
910.0	93.983	7.645
938.1	94.310	0.326
950.7	94.369	0.059
970.1	94.453	0.085
988.2	94.499	0.046
1001.9	94.572	0.070
1011.0	94.631	0.058
1020.0	94.757	0.126
1030.7	94.809	0.052
1054.1	96.353	1.543
1070.6	98.434	2.080
1082.1	98.555	0.120
1112.8	98.569	0.014
1125.7	98.669	0.100
1148.0	98.783	0.094
1157.4	98.857	0.075
1169.1	99.954	0.096
1180.4	99.206	0.250
1192.1	99.323	0.118
1200.8	99.345	0.021
1223.8	99.381	0.036
1247.1	99.327	0.053
1272.1	99.540	0.213
1279.1	99.566	0.026
1295.9	99.572	0.005
1298.7	99.579	0.007
1309.3	99.599	0.020
1316.8	99.613	0.014
1339.9	99.920	0.307
1641.2	99.922	0.001
1677.1	99.923	0.001
1764.8	99.925	0.001
1851.8	99.928	0.003
1875.1	99.929	0.001
1708.3	99.931	0.002
1720.3	99.933	0.001
1747.3	99.934	0.001
1760.3	99.935	0.001
1778.2	99.936	0.001
1781.4	99.938	0.002
1933.3	99.942	0.004
1950.7	99.944	0.002
1977.8	99.947	0.003
1993.7	99.949	0.002
2008.8	99.950	0.001
2113.8	99.951	0.001
2311.1	99.952	0.001
2419.8	100.000	0.048

TBP DISTILLATION ANALYSIS
ARD ANALYTICAL
OPERATIONS
FROM R.A.ERSEK D-147 EXT. 5229

PROJECT NUMBER	DATE RUN	SAMPLE NUMBER	DESCRIPTION OF SAMPLE	SIZE (MLS.)	SUBMITTED BY	NOTEBOOK PAGE NO.
48-509	10-25-78	#10-13(1)V	HEATED DCPD	3000	H.K.MYERS	778409

Cut #	Atmos. TEMP.	WT. GMS.	VOL. MLS.	SP.GR.60/60 F	WT.PCT.	VOL.PCT.
	341		0		0.0	0.0
	456		200		7.7	8.7
	463		250		9.7	10.8
	480		400		15.5	17.4
	492		500		19.4	21.7
	505		600		23.3	26.1
	526		700		27.2	30.4
	527		750		29.1	32.6
1	527	758.9		1.0039	29.1	32.6
	547		250		39.4	43.4
	567		400		45.5	49.9
	572		500		49.6	54.2
	586		600		53.7	58.5
2	586	639.9		1.0645	24.6	25.9
	615		150		60.2	65.3
	629		200		62.4	67.6
	659		320		67.5	73.0
3	659	358.9		1.0694	13.8	14.4
4	659	842.9		>1.1376 <1.3519	32.4	26.9
	TOTAL	2600.9		1.1228		
	CHARGE	2780.9		1.0668	100.0	100.0
	LOSS	180.0				

Maximum vacuum: .4mmHg during distillation

Chart #6

TBP DISTILLATION ANALYSIS AND ANALYTICAL OPERATIONS

FROM R.A.ERSEK D-147 EXT. 5229

PROJECT NUMBER	DATE RUN	SAMPLE NUMBER	DESCRIPTION OF SAMPLE	SIZE (MLS.)	SUBMITTED BY	NOTEBOOK PAGE NO.
		HKM 11-9-78(1)				
Cut # 48-509 Atmos.	11-08-78	#743122-1	HEATED DCPD	5300	E.JANOSKI	773417

	TEMP.	WT. GMS.	VOL. MLS.	SP.GR.60/60 F	WT.PCT	VOL.PCT.
	425		0		0.0	0.0
	473		900		17.0	18.7
	473		1050		19.8	21.8
1	473	1008.9		0.9915	19.8	21.8
2	504		350		26.8	29.3
	504	353.9		1.0120	6.9	7.5
	517		300		33.0	35.7
	523		400		35.1	37.8
	534		720		41.7	44.7
3	543		810		43.5	46.6
	543	847.9		1.0511	16.7	17.7
	554		250		48.7	51.9
	564		475		53.4	56.6
4	564	500.0		1.0675	9.8	10.0
	575		225		58.0	61.3
5	575	233.9		1.0722	4.6	4.6
6	609		210		62.4	65.8
	609	223.9		1.0706	4.4	4.4
	617		140		65.4	68.8
7	617	149.9		1.0699	2.9	3.0
8	617	(Upper phase of Cut #7)	220		70.0	73.5
	617	235.0		1.0639	4.6	4.7
	617		110		72.3	75.8
9	617	113.9		1.0499	2.2	2.3
Bottoms	617	1404.9		1.2500	27.6	24.1
	TOTAL CHARGE	5073.9 5320.0		1.0880 1.0450	100.0	100.0
	LOSS	256.0				

Maximum vacuum: .4mm Hg during distillation

Chart #7

CHART 6 MKM 11-29-78 (1) Residual Isomerized THTriCPD after settling overnight on $AlCl_3$

PROCEED
CALLING PROGRAM CALPT-MAX. NO. OF PEAKS=300
M.S. NUMBER = 1253
Mass PATT DIV Mass Spectrograph ran at 8.5 volts

76	0.1	2.	131	[illegible]	[illegible]	192	0.0	1.	259	0.2	5.
77	0.1	2.	[illegible]	[illegible]	[illegible]	194	0.1	3.	260	0.1	2.
78	0.4	9.	133	[illegible]	220.	195	0.2	4.	262	0.1	3.
79	0.1	3.	136	38.6	791.	196	0.8	16.	263	0.0	1.
80	4.7	98.	135	18.1	183.	197	0.2	4.	264	0.3	6.
81	3.3	18.	138	11.5	264.	198	2.3	41.	265	0.0	1.
82	0.1	1.	137	1.3	11.	199	0.9	19.	266	1.6	34.
83	0.0	1.	138	0.2	5.	200	5.7	117.	267	0.9	18.
84	0.4	9.	139	0.0	0.	201	4.2	88.	268	4.5	92.
85	0.0	1.	141	0.0	1.	202	100.0	2049.	269	1.9	40.
86	0.2	6.	142	0.5	12.	203	28.9	592.	270	4.4	91.
87	0.0	1.	143	0.1	2.	204	24.1	494.	271	1.4	28.
88	0.0	1.	144	0.4	9.	205	5.4	112.	272	1.3	27.
90	0.0	0.	145	0.5	10.	206	1.8	38.	277	0.0	1.
91	0.2	4.	146	0.5	11.	208	0.0	1.	278	0.6	13.
92	0.7	15.	147	0.6	13.	210	1.2	24.	279	0.0	1.
93	0.9	19.	148	3.0	63.	211	0.3	7.	280	0.6	12.
94	2.4	50.	149	0.4	8.	212	0.3	7.	281	0.3	6.
95	5.2	107.	152	0.1	2.	213	0.5	11.	284	0.1	3.
96	0.4	8.	154	2.1	44.	214	0.7	16.	286	0.1	2.
97	0.1	2.	155	0.2	5.	215	0.3	6.	289	0.0	1.
98	0.0	1.	156	1.9	40.	216	0.7	14.	290	0.0	1.
99	0.0	1.	157	0.3	7.	218	0.5	11.	292	0.1	2.
100	0.0	1.	158	0.1	2.	219	0.2	5.	293	0.1	2.
101	0.0	1.	159	2.4	50.	221	0.1	3.	295	0.0	1.
102	0.0	1.	160	3.1	63.	224	0.2	4.	301	0.0	0.
103	0.0	0.	161	9.3	191.	225	0.2	4.	302	0.0	1.
104	0.2	5.	162	1.8	38.	227	0.3	7.	303	0.0	0.
105	0.2	5.	163	0.2	5.	228	0.3	8.	304	0.0	1.
106	2.1	43.	164	0.0	1.	229	0.3	7.	306	0.0	1.
107	1.6	34.	165	0.0	1.	231	0.1	3.	307	0.1	3.
108	1.7	36.	168	0.2	4.	232	0.2	5.	308	0.1	2.
109	0.5	10.	169	0.0	1.	233	0.1	3.	313	0.0	1.
110	0.2	4.	170	0.9	19.	235	0.3	7.	316	0.0	1.
111	0.1	2.	171	0.3	6.	237	0.1	2.	319	0.1	2.
112	0.1	3.	172	0.4	8.	238	0.2	4.	320	0.0	1.
113	0.0	1.	173	5.1	106.	239	0.0	1.	321	0.0	1.
115	0.0	1.	174	7.2	148.	240	0.2	5.	322	0.1	3.
116	0.0	1.	175	3.6	75.	241	0.5	10.	329	0.0	1.
117	0.1	2.	176	2.0	42.	242	0.2	4.	332	0.2	4.
118	1.3	28.	177	0.5	10.	243	0.2	5.	333	0.4	1.
119	2.3	48.	178	0.1	2.	244	0.1	3.	334	0.2	4.
120	10.6	217.	179	0.0	0.	246	0.0	1.	335	0.1	3.
121	5.3	108.	182	0.1	2.	248	0.0	1.	336	0.6	12.
122	2.0	42.	184	0.1	3.	249	0.0	1.	337	0.3	7.
123	0.9	19.	185	0.0	0.	250	0.0	1.	338	0.5	11.
124	0.2	4.	186	0.2	6.	251	0.0	1.	340	0.2	4.
125	0.1	3.	187	1.2	25.	253	0.0	1.	341	0.0	0.
127	0.0	1.	188	0.5	10.	254	0.1	2.	343	0.4	9.
128	0.1	2.	189	3.9	81.	255	0.1	3.	345	0.0	1.
132	0.0	1.	190	1.0	21.	256	0.0	1.	347	0.0	1.
									348	0.0	1.
									349	0.0	0.
									350	0.1	3.

CHART 9 HKM 11-30-78 (1) Final Isomerized THTriCPD

PROCEED
CALLING PROGRAM CALPT-MAX. NO. OF PEAKS=300
M.S. NUMBER = 1252
Mass Spectrograph ran at 8.5 volts

Mass	PATT	DIV	Mass	PATT	DIV	Mass	PATT	DIV	Mass	PATT	DIV
63	0.0	1.	109	0.5	12.	162	2.4	54.	214	0.1	3.
64	0.1	3.	110	0.1	3.	163	0.6	14.	215	0.0	1.
65	0.1	3.	111	0.1	2.	164	0.0	2.	216	0.2	5.
66	5.1	112.	112	0.1	2.	165	0.0	1.	217	0.4	9.
67	1.3	29.	113	0.1	2.	166	0.1	2.	218	0.3	7.
68	0.6	13.	114	0.1	2.	167	0.0	2.	222	0.1	3.
69	0.4	9.	116	0.0	1.	168	0.0	1.	223	0.2	4.
71	0.0	1.	117	0.1	4.	170	0.6	14.	224	0.2	5.
70	0.0	1.	118	1.9	42.	171	0.2	4.	226	0.3	7.
71	0.0	1.	119	3.4	75.	172	0.2	4.	227	0.6	13.
73	0.0	1.	120	13.0	287.	173	6.5	144.	229	0.5	11.
74	0.0	1.	121	6.4	142.	174	9.6	211.	230	0.2	5.
75	0.0	1.	122	2.4	54.	175	2.8	62.	231	0.4	9.
76	0.0	1.	123	1.0	23.	176	0.9	20.	232	0.2	5.
77	0.0	1.	124	0.2	5.	177	0.1	4.	234	0.2	4.
78	0.3	8.	125	0.1	2.	178	0.0	1.	236	0.2	5.
79	0.2	4.	127	0.0	1.	180	0.1	2.	238	0.3	7.
80	5.7	127.	128	0.1	3.	181	0.0	0.	239	0.3	7.
81	1.0	23.	130	0.0	1.	182	0.1	3.	240	0.7	17.
82	0.1	2.	131	0.3	6.	184	0.2	4.	241	0.3	8.
83	0.0	2.	132	3.4	75.	185	0.4	9.	242	0.2	5.
84	0.0	2.	133	12.3	272.	186	0.3	7.	243	0.3	7.
85	0.1	2.	134	50.6	1116.	187	1.3	30.	244	0.2	5.
86	0.2	5.	135	24.4	539.	188	0.3	7.	246	0.2	4.
87	0.1	2.	136	12.8	282.	189	2.0	45.	247	0.1	3.
88	0.2	5.	137	1.6	37.	190	0.7	16.	249	0.1	4.
89	0.2	6.	138	0.3	6.	194	0.0	1.	250	0.2	5.
90	0.2	5.	140	0.1	2.	195	0.2	5.	251	0.2	5.
91	0.4	10.	142	0.7	17.	196	0.2	4.	252	0.2	4.
92	1.0	23.	143	0.0	2.	197	0.1	2.	255	0.2	5.
93	1.2	28.	144	0.0	1.	198	0.1	2.	256	0.2	6.
94	2.7	61.	145	0.6	13.	199	0.3	7.	257	0.2	4.
95	5.8	128.	146	0.8	18.	200	1.4	32.	258	0.1	4.
96	0.7	17.	147	1.1	24.	201	2.3	51.	259	0.2	4.
97	0.1	4.	148	3.6	79.	202	100.0	2205.	261	0.1	3.
98	0.1	3.	149	0.8	19.	203	26.9	594.	262	0.1	3.
99	0.1	3.	153	0.0	1.	204	14.6	321.	263	0.2	4.
101	0.0	0.	154	3.4	76.	205	3.2	70.	266	0.7	16.
102	0.0	2.	155	0.6	13.	206	0.8	17.	267	0.4	10.
103	0.0	1.	156	2.4	53.	207	0.1	2.	268	6.0	133.
104	0.3	7.	157	0.5	11.	208	0.0	0.	269	2.4	53.
105	0.2	5.	158	0.2	4.	209	0.0	0.	270	2.7	60.
106	2.5	56.	159	3.4	76.	210	1.4	31.	272	0.7	16.
107	1.9	43.	160	4.2	92.	211	0.2	5.	274	0.2	5.
108	2.0	45.	161	11.5	255.	212	0.0	1.	276	0.1	4.
									277	0.2	5.
									279	0.1	3.
									280	0.2	5.

Chart 10 HKM 12-11-78 (1) Isomerized THTriCPD

PROCEED
CALLING PROGRAM CALPT-MAX. NO. OF PEAKS=300
M.S. NUMBER = 1333
MASS PATT. DIV Mass Sp-ctrograph ran at 8.5 Volts

64	0.1	1.		108	2.0	34.		158	0.4	7.		214	0.8	13.		
65	0.2	3.		109	0.7	12.		159	3.6	63.		215	0.4	8.		
66	4.6	78.		110	0.4	8.		160	5.1	88.		216	0.7	12.		
67	1.4	25.		111	0.2	4.		161	12.2	208.		218	0.4	8.		
68	0.6	10.		112	0.6	11.		162	2.6	45.		219	0.3	5.		
69	0.3	6.		113	0.2	4.		163	0.4	7.		220	0.3	5.		
70	0.4	7.		115	0.0	1.		164	0.1	2.		221	0.2	4.		
71	0.3	5.		116	0.0	1.		165	0.0	0.		222	0.3	5.		
72	0.2	3.		117	0.2	3.		167	0.3	5.		224	0.3	6.		
73	0.1	2.		118	2.2	38.		168	0.6	11.		225	0.4	6.		
74	0.1	1.		119	3.6	62.		169	0.4	7.		226	0.5	9.		
75	0.6	1.		120	14.8	252.		170	0.9	15.		227	1.7	29.		
76	0.1	3.		121	5.8	100.		17	0.5	09.		228	0.7	12.		
77	0.0	1.		122	2.5	42.		172	0.8	14.		230	0.2	4.		
78	0.5	8.		123	0.9	16.		173	7.5	128.		235	0.2	4.		
79	0.1	3.		124	0.2	3.		174	10.7	183.		236	0.3	6.		
80	5.6	96.		125	0.0	1.		175	3.4	59.		237	0.3	6.		
81	1.0	17.		126	0.1	2.		176	1.4	24.		238	0.7	12.		
82	0.2	4.		127	0.0	1.		177	0.5	9.		239	0.6	11.		
83	0.2	3.		128	0.1	2.		182	0.3	5.		240	1.7	30.		
84	1.1	20.		129	0.1	2.		183	0.3	5.		241	1.3	23.		
85	0.2	3.		130	0.1	2.		184	0.3	6.		242	0.7	12.		
86	0.8	15.		131	0.4	7.		185	0.4	8.		243	0.5	9.		
87	0.1	1.		132	4.0	69.		186	1.5	25.		244	0.4	7.		
88	0.1	2.		133	14.1	241.		187	2.2	38.		245	0.2	4.		
89	0.1	2.		134	53.0	906.		188	0.9	16.		250	0.4	8.		
90	0.0	0.		135	24.1	411.		189	2.4	42.		251	0.7	12.		
91	0.2	4.		136	6.6	113.		190	1.0	17.		252	0.5	8.		
92	1.0	17.		137	0.7	13.		193	0.2	4.		253	0.4	7.		
93	1.1	19.		138	0.0	1.		195	0.3	5.		255	0.5	8.		
94	2.1	36.		140	0.0	0.		196	0.6	10.		256	0.5	8.		
95	5.1	87.		141	0.0	1.		197	0.5	9.		259	0.2	4.		
96	0.4	8.		142	0.6	11.		198	1.5	26.		262	0.3	6.		
97	0.1	1.		143	0.1	2.		199	2.3	39.		264	0.8	14.		
98	0.1	1.		145	0.6	10.		200	6.9	119.		265	0.5	9.		
99	0.0	1.		146	1.3	22.		201	7.7	131.		266	6.0	102.		
100	0.0	1.		147	1.2	21.		202	100.0	1707.		267	2.7	46.		
101	0.0	1.		148	3.9	67.		203	28.7	490.		268	26.4	450.		
102	0.0	0.		149	0.9	16.		204	15.8	271.		269	9.8	168.		
103	0.0	1.		153	0.0	1.		205	3.8	65.		270	8.9	153.		
104	0.5	9.		154	0.2	3.		206	1.3	23.		271	3.0	51.		
105	0.5	8.		155	0.0	1.		209	0.2	4.		272	2.1	37.		
106	3.3	56.		156	2.4	42.		210	0.4	7.		273	0.8	14.		
107	2.1	35.		157	0.4	8.		213	0.3	6.		275	0.3	5.		
												278	0.3	6.		
												280	0.6	11.		

Chart 11 HKM 1-4-79 (1) Isomerized THTriCPD

PROCEED
CALLING PROGRAM CALPT-MAX. NO. OF PEAKS=300
M.S. NUMBER = 1484
MASS PATT DIV Mass Spectrograph ran at 8.5 Volts

60	0.1	2.	I	105	0.4	5.	I	155	0.3	5.	I	214	0.7	9.
61	0.1	1.	I	106	2.2	31.	I	156	0.2	3.	I	216	0.7	10.
62	0.1	1.	I	107	1.3	19.	I	158	0.4	6.	I	218	0.6	8.
63	0.1	1.	I	108	1.3	18.	I	159	2.9	41.	I	219	0.4	6.
64	0.1	1.	I	109	0.4	5.	I	160	3.7	52.	I	221	0.3	4.
65	0.1	2.	I	110	0.2	3.	I	161	9.8	138.	I	222	0.9	13.
66	2.1	29.	I	111	0.2	2.	I	162	2.2	31.	I	223	0.5	7.
67	0.5	7.	I	113	0.2	3.	I	165	0.3	4.	I	226	1.0	15.
68	0.3	4.	I	114	0.2	2.	I	166	0.3	4.	I	227	0.6	9.
69	0.2	3.	I	115	0.1	2.	I	168	0.3	5.	I	229	0.6	9.
70	0.2	3.	I	116	0.0	0.	I	169	0.3	5.	I	230	0.5	6.
71	0.1	1.	I	117	0.2	4.	I	170	0.3	5.	I	231	0.4	6.
72	0.1	2.	I	118	1.7	24.	I	172	0.5	7.	I	234	0.4	6.
73	0.1	2.	I	119	2.6	36.	I	173	5.8	81.	I	235	0.4	6.
74	0.0	0.	I	120	10.6	148.	I	174	8.1	114.	I	236	0.5	7.
75	0.0	1.	I	121	4.2	59.	I	175	2.7	38.	I	237	0.5	7.
76	0.1	1.	I	122	1.8	25.	I	176	1.2	17.	I	238	0.6	8.
77	0.1	1.	I	123	0.8	11.	I	177	0.4	5.	I	240	1.3	18.
78	0.2	4.	I	124	0.0	0.	I	179	0.3	4.	I	241	1.3	19.
79	0.1	2.	I	127	0.0	1.	I	180	0.5	7.	I	242	1.3	19.
80	3.4	48.	I	128	0.1	2.	I	183	0.3	5.	I	245	0.4	6.
81	0.6	8.	I	130	0.1	1.	I	184	0.3	5.	I	246	0.5	7.
82	0.3	4.	I	131	0.2	3.	I	186	0.8	11.	I	247	0.4	5.
83	0.2	2.	I	132	2.8	39.	I	187	1.7	23.	I	252	0.5	7.
84	0.6	8.	I	133	10.4	145.	I	188	0.7	10.	I	253	0.5	8.
85	0.1	1.	I	134	42.5	595.	I	189	2.6	36.	I	254	0.8	11.
86	0.5	7.	I	135	19.4	271.	I	190	0.9	13.	I	255	0.6	9.
87	0.1	1.	I	136	7.5	106.	I	191	0.4	6.	I	256	0.4	6.
88	0.1	2.	I	137	0.8	12.	I	193	0.3	4.	I	259	0.4	6.
89	0.2	3.	I	138	0.0	1.	I	194	0.4	6.	I	260	0.4	6.
90	0.2	3.	I	139	0.1	1.	I	196	0.6	9.	I	261	0.7	9.
91	0.4	6.	I	140	0.3	4.	I	198	1.4	19.	I	264	1.2	17.
92	0.9	12.	I	142	0.2	4.	I	199	1.2	17.	I	265	0.8	11.
93	0.8	12.	I	143	0.2	3.	I	200	4.7	66.	I	266	3.4	48.
94	1.6	23.	I	144	0.3	4.	I	201	4.8	68.	I	267	1.4	20.
95	3.7	52.	I	145	0.8	11.	I	202	100.0	1398.	I	268	16.7	234.
96	0.6	8.	I	146	1.0	14.	I	203	24.1	337.	I	269	5.7	80.
97	0.3	4.	I	147	1.1	15.	I	204	15.4	215.	I	270	9.8	137.
98	0.3	4.	I	148	3.6	51.	I	205	3.4	47.	I	271	3.1	43.
100	0.2	3.	I	149	1.1	16.	I	206	1.4	19.	I	272	2.2	32.
101	0.1	2.	I	150	0.6	9.	I	208	1.0	14.	I	276	0.4	6.
102	0.1	1.	I	152	0.5	6.	I	210	0.2	3.	I	277	0.2	3.
103	0.0	1.	I	153	0.2	3.	I	211	0.3	4.	I	278	0.5	7.
104	0.4	5.	I	154	0.2	3.	I	212	0.4	6.	I	277	0.5	7.
											I	279	0.6	9.
											I	280	0.7	10.
											I	281	0.7	9.

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